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Review of Criteria for Vapor-Phase Hydrocarbons

B. E. Tilton, et al

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16. ABSTRACT

Information on vapor-phase hydrocarbons presented in this document covers basic atmospheric chemistry relative to secondary products, especially ozone; sources and emissions; ambient air concentrations; relationship of precursor hydrocarbons to resultant ozone levels in ambient air; health effects; and welfare effects. The principal conclusions from this document are as follows. Hydrocarbons are a principal contributor to the formation of ozone and other photochemical oxidants; however, no fixed single quantitative relationship between precursor hydrocarbons and resulting ozone concentrations can be defined. This relationship varies from site to site depending on local precursor mixes, transport considerations, and meteorological factors. Consequently no single quantitative relationship can be defined nationwide. While specific hydrocarbon compounds can be of concern to public health and welfare, as a class this group of materials cannot be considered a hazard to human health or welfare at or even well above those concentrations observed in the ambient air.

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by

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FOREWORD

This document has been prepared pursuant to Section 108(c) of the Clean Air Act, as amended, which requires that the Administrator from time to time review and, as appropriate, modify and reissue criteria issued pursuant to Section 108(a). Air quality criteria are required by Section 108(a) to reflect accurately the latest scientific information useful in indicating the kind and extent of all identifiable effects on public health and welfare that may be expected from the presence of a pollutant in the ambient air in varying quantities.

The original criteria document for hydrocarbons, AP-64, was issued in 1970. Since that time, new information has been developed, and this document represents the review and revision of pertinent air quality criteria for hydrocarbons.

The regulatory purpose of this review is to serve as the basis for national ambient air quality standards promulgated by the Administrator under Section 109 of the Clean Air Act, as amended. Accordingly, as provided by Section 109(d), the Administrator has reviewed the national ambient air quality standards for hydrocarbons based on this review of criteria and literature since 1970 and is proposing appropriate action with respect to those standards concurrently with the issuance of this document.

The Agency is pleased to acknowledge the efforts and contributions of all persons and groups who have contributed to this document as participating authors or reviewers. In the last analysis, however, the Environmental Protection Agency is responsible for its content.

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TABLE OF CONTENTS

Page

FIGURES.......... xiii
TABLES.......... xiv
ABSTRACT.......... xvii

1. SUMMARY AND CONCLUSIONS.......... 1-1
  1.1 INTRODUCTION.......... 1-1
  1.2 BACKGROUND INFORMATION.......... 1-3
  1.3 CONTRIBUTION OF HYDROCARBONS TO OXIDANT FORMATION.......... 1-8
  1.4 MEASUREMENT METHODOLOGY.......... 1-9
  1.5 SOURCES AND EMISSIONS.......... 1-10
  1.6 AMBIENT AIR CONCENTRATIONS.......... 1-12
  1.7 HYDROCARBON/OXIDANT RELATIONSHIP.......... 1-15
  1.8 HEALTH AND WELFARE EFFECTS OF HYDROCARBONS.......... 1-18

2. RECOMMENDATIONS.......... 2-1

3. INTRODUCTION.......... 3-1
  3.1 BASIS FOR AIR QUALITY CRITERIA AND NATIONAL AMBIENT AIR QUALITY STANDARDS.......... 3-1
  3.2 BASIS AND NATURE OF PRESENT REVIEW OF CRITERIA FOR HYDROCARBONS.......... 3-2

4. BACKGROUND INFORMATION.......... 4-1
  4.1 UNIQUE CHARACTERISTICS OF CRITERIA AND STANDARDS FOR HYDROCARBONS.......... 4-1
  4.2 NEED FOR A CRITERIA DOCUMENT FOR HYDROCARBONS.......... 4-3

5. SUMMARY OF 1970 CRITERIA FOR HYDROCARBONS.......... 5-1
  5.1 CONTRIBUTION OF HYDROCARBONS TO FORMATION OF PHOTOCHEMICAL OXIDANTS.......... 5-1
  5.2 MEASUREMENT METHODOLOGY.......... 5-4
  5.3 SOURCES AND EMISSIONS OF HYDROCARBONS.......... 5-7
  5.4 AMBIENT AIR CONCENTRATIONS.......... 5-8
  5.5 HYDROCARBON/OXIDANT RELATIONSHIPS.......... 5-17
  5.6 HEALTH EFFECTS.......... 5-23
    5.6.1 Aliphatic Hydrocarbons.......... 5-26
    5.6.2 Alicyclic Hydrocarbons.......... 5-26
    5.6.3 Aromatic Hydrocarbons.......... 5-30
    5.6.4 Hydrocarbon Mixtures.......... 5-32
  5.7 WELFARE EFFECTS.......... 5-38

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Page

6. SCIENTIFIC DATA BASE ON HYDROCARBONS, 1970 THROUGH PRESENT....... 6-1
  6.1 CONTRIBUTION OF HYDROCARBONS TO OXIDANT FORMATION.......... 6-1
  6.2 MEASUREMENT METHODOLOGY.................................... 6-8
  6.3 SOURCES AND EMISSIONS OF HYDROCARBONS...................... 6-19
    6.3.1 General... 6-19
    6.3.2 Natural Sources and Emissions....................... 6-31
    6.3.3 Manmade Sources and Emissions....................... 6-39
  6.4 AMBIENT AIR CONCENTRATIONS................................. 6-94
  6.5 HYDROCARBON-OZONE RELATIONSHIP............................. 6-131
    6.5.1 Factors Affecting the Hydrocarbon-ozone Relationship. 6-135
    6.5.2 Models for Determining Hydrocarbon Emission Reductions... 6-144
  6.6 HEALTH EFFECTS... 6-149
    6.6.1 Aliphatic Hydrocarbons.............................. 6-150
    6.6.2 Alicyclic Hydrocarbons.............................. 6-153
    6.6.3 Aromatic Hydrocarbons............................... 6-159
    6.6.4 Hydrocarbon Mixtures--Gasoline...................... 6-163
    6.6.5 Miscellaneous Hydrocarbons.......................... 6-167
    6.6.6 Health Effects Summary.............................. 6-170
  6.7 WELFARE EFFECTS.. 6-176
    6.7.1 Welfare Effects Summary............................. 6-182
7. REFERENCES... 7-1

LIST OF FIGURES

Figure ... Page

5-1 Nonmethane hydrocarbons by flame ionization analyzer, averaged by hour of day over several months for four cities.............. 5-16
5-2 Hourly aldehyde concentrations at two Los Angeles sites, October 22, 1968... 5-19
5-3 Maximum daily oxidant as a function of early morning nonmethane hydrocarbons, 1966-1968, for CAMP stations; May through October 1967 for Los Angeles.. 5-21
5-4 Required hydrocarbon emission control as a function of photochemical oxidant concentration............................ 5-24
6-1 Density of population in U.S. in 1975 by state, no. people/mi.^{2}.. 6-24
6-2 Density of total nonmethane hydrocarbon emissions in U.S. in 1975 by state, tons/mi.^{2}...................................... 6-25
6-3 Effects of fuel composition on THC and ethanol emission rates.... 6-80
6-4 Distribution of diesel hydrocarbon exhaust emissions, by molecular weight, between gas-phase and particulate forms................. 6-84
6-5 Distribution of hydrocarbons in diesel fuel and lubricant according to molecular weight.................................. 6-85
6-6 Nonmethane hydrocarbon trends in Los Angeles, 1963 through 1972.. 6-100
6-7 Sum of nonmethane hydrocarbon concentrations versus number of samples for two ground sites used in the 1974 Midwest Oxidant Transport Study... 6-110
6-8 Occurrence of gas-phase hydrocarbons, by carbon number, in gasoline, exhaust, and urban ambient air....................... 6-132
6-9 Calculated gasoline threshold limit value, reflecting impact of present vs. newly promulgated TLV standard as a function of the liquid volume percent benzene in the gasoline............ 6-168
6-10 Geographic location of the grab sample collection sites......... 6-179

LIST OF TABLES

Table		Page
5-1	Some hydrocarbons identified in ambient air	5-10
5-2	Average hydrocarbon compositon, 218 ambient air samples, Los Angeles, 1965	5-12
5-3	Average and highest concentration measured for various aromatic hydrocarbons in Los Angeles, 26 days, September through November, 1966	5-13
5-4	Range of yearly maximum 1-hour average concentrations of aldehydes, Los Angeles County stations, 1951 through 1957	5-15
5-5	Average formaldehyde and acrolien concentrations by time of day in Los Angeles, September 25 through November 15, 1961	5-18
5-6	Toxicity of saturated aliphatic hydrocarbons	5-27
5-7	Toxicity of unsaturated aliphatic hydrocarbons	5-29
5-8	Toxicity of alicyclic hydrocarbons: Comparative effects of chronic and acute exposure in air	5-31
5-9	Toxicity of aromatic hydrocarbons: Comparative effects of acute and chronic exposure in air	5-33
5-10	Principal mixtures containing paraffin hydrocarbons	5-37
5-11	Human response to gasoline vapors distilling below 230°F	5-39
5-12	Comparative phytotoxicity of unsaturated carbon gases	5-41
5-13	Dosage-response relationships of various plants to ethylene	5-43
5-14	American Industrial Hygiene Association recommended standards for ethylene	5-44
6-1	Possible atmospheric gas phase SO_2 oxidation processes	6-7
6-2	Percentage difference from known concentrations of nonmethane hydrocarbons obtained by sixteen users	6-9
6-3	Summary of national estimates of volatile organic emissions, 1970-1977	6-21
6-4	National estimates of volatile organic emissions, 1977, by source category	6-22
6-5	Comparison of selected Houston emission rate and ambient air data	6-34
6-6	Comparison of Houston and Tampa/St. Petersburg TNMHC emission rates	6-35
6-7	Biogenic HC emission rates at constant environmental conditions	6-37
6-8	Comparison of monoterpene emissions from various plant species	6-38
6-9	Emissions of volatile organic compounds from stationary external combustion sources	6-41
6-10	Emissions of volatile organic compounds from stationary source internal combustion engines	6-42
6-11	Emissions of volatile organic compounds from manufacture of selected chemicals/products	6-44
6-12	Emissions of volatile organic compounds from sanitary landfills	6-45
6-13	Emissions of volatile organic compounds from general use of domestic solvents	6-47
6-14	Emissions of volatile organic compounds from domestic and commercial use of pesticides	6-48

Table Page

6-15 Emissions of volatile organic compounds from the use of architectural surface coatings.................................... 6-50
6-16 Emissions of volatile organic compounds from forest fires and from open burning of agricultural/landscape wastes............... 6-51
6-17 Hydrocarbon emissions from agricultural burning of field and orchard crop residues.. 6-52
6-18 Nationwide estimates of VOC emissions from transportation sources, 1970 through 1977.. 6-54
6-19 Hydrocarbon exhaust emission factors for light-duty, gasoline-powered vehicles for all areas except California and high-altitude.. 6-56
6-20 Composite crankcase and evaporative emission factors for light-duty, gasoline-powered vehicles for all areas except California and high-altitude.. 6-56
6-21 General Motors Corporation systems for control of hydrocarbon and other pollutant emissions.................................. 6-57
6-22 Summary data on gasoline composition, reported as weight percent. 6-62
6-23 Average gasoline vapor composition................................ 6-63
6-24 Predominant hydrocarbons in exhaust emissions from gasoline-fueled autos... 6-65
6-25 Summary of exhaust emission data for uncontrolled and catalyst-equipped gasoline-fueled cars by model year.................... 6-67
6-26 Exhaust, evaporative, and aggregate emissions of total hydrocarbons, benzene, and toluene from four passenger cars (1963 through 1979 model years) and four fuels.......................... 6-73
6-27 Increase in exhaust emission rates of aromatic aldehyde for non-catalyst gasoline cars with increase in fuel aromaticity..... 6-74
6-28 Total hydrocarbon emission rates on (ECE test cycle) for car fueled with gasoline, methanol, or a 15% methanol-85% gasoline mixture.. 6-75
6-29 Exhaust emissions from vehicle equipped with three-way conversion catalyst and fueled with gasoline, ethanol-gasoline, or methanol-gasoline.. 6-77
6-30 Test fuel specifications... 6-79
6-31 Emission rates for hydrocarbons in exhaust from two diesel vehicles... 6-86
6-32 Aldehyde emissions from diesel vehicles operating on five different fuels, 1975 FTP.. 6-89
6-33 Summary of reactivity of diesel exhaust hydrocarbon emissions and percentage contributions of lower-molecular-weight hydrocarbons and aldehydes.. 6-91
6-34 Summary of emission characteristics for autos fueled by gasoline diesel and alcohol-gasoline or ether-gasoline blends............ 6-92
6-35 Ambient air concentrations of hydrocarbons reported by Graedel... 6-96
6-36 Frequency distributions for 6-to-9 a.m. nonmethane hydrocarbon concentrations at CAMP sites, 1967-1972.......................... 6-99
6-37 Trends in 6-to-9 a.m. concentrations of indicator hydrocarbons at two sites in the California South Coast Air Basin, 1967 through 1977.. 6-102

Table

6-38 Maximum and average 6-to-9 a.m. nonmethane hydrocarbon concentrations at four sites in California South Coast Air Basin, June through September 1975 6-103
6-39 Total nonmethane hydrocarbon concentrations in 2-hour samples measured by gas chromatography at urban site in St. Louis for 6 days, September 13-25, 1972 6-105
6-40 Total nonmethane hydrocarbon concentrations in 2-hour samples measured by gas chromatography at urban site in St. Louis for 4 days, June 21-July 8, 1973 6-106
6-41 24-hour average hydrocarbon concentrations measured by gas chromatography at urban site in St. Louis, September 13, 1972 6-107
6-42 24-hour average individual hydrocarbon measurements at Wilmington, Ohio, July 18, 1974, determined by gas chromatography 6-111
6-43 Concentrations of total nonmethane hydrocarbons, methane, and selected oxygenates in eleven 2-hour and two 1-hour samples taken over 24 hours, July 18, 1974, Wilmington, Ohio 6-113
6-44 Concentrations of natural hydrocarbons in ambient air samples taken within and outside a forest conopy 6-115
6-45 24-hour average individual hydrocarbon concentrations measured by gas chromatography, Boston area, 1975 6-117
6-46 Total nonmethane hydrocarbon concentrations in Houston by time of day for 23 days, July 3-25, 1976, determined by FID 6-120
6-47 Concentrations of hydrocarbons by class in air samples collected at 19 sites in Houston, 1973 and 1974, determined by gas chromatography 6-121
6-48 Concentrations of individual hydrocarbons in air samples collected in Houston on September 11, 1973, determined by gas chromatography 6-122
6-49 Average percentage composition of hydrocarbons in ambient air at selected sites in Houston (1978) and St. Louis (1972 and 1977) 6-to-9 a.m. period 6-126
6-50 Effect of wind direction on hydrocarbon composition at site 03, Houston 6-127
6-51 Average concentrations of benzene in ambient air at four California sites, Summer 1975 6-130
6-52 Mean values and ranges in aromatic hydrocarbon concentrations in West Germany, July 1976 6-131
6-53 Some factors that affect the photochemical formation of ozone from precursors 6-136
6-54 Comparison of reactivities of different types of organics 6-141
6-55 Classification of organics with respect to oxidant-related reactivity in urban atmospheres 6-143
6-56 Effects of alkane vapor pressure on humans 6-154
6-57 Effects of alkane vapor pressure on animals 6-156
6-58 Human experience: exposure to gasoline vapors 6-166
6-59 Suggested hygienic standard for various hydrocarbon solvent mixtures based on inhalation toxicity studies of animals and sensory response of human subjects 6-171
6-60 Houston study ethylene levels 6-178

ABSTRACT

Information on vapor-phase hydrocarbons presented in this document covers basic atmospheric chemistry relative to secondary products, especially ozone; sources and emissions; ambient air concentrations; relationship of precursor hydrocarbons to resultant ozone levels in ambient air; health effects; and welfare effects.

The principal conclusions from this document are as follows. Vapor-phase hydrocarbons, along with many other volatile organic compounds, contribute to the formation of ozone and other photochemical oxidants. The relationship between precursor hydrocarbons and consequent ambient air levels of ozone and other oxidants is complex, however, and varies from site to site, city to city, and year to year, depending on local precursor mixes, transport considerations, and meteorological factors. Consequently, no single quantitative relationship between hydrocarbons and ozone/oxidants can be defined nationwide.

While specific vapor-phase hydrocarbon compounds can be of concern to public health (benzene) and welfare (ethylene), as a class, this group of compounds cannot be considered a hazard to human health or welfare at or even well above those concentrations observed in the ambient air.

1. SUMMARY AND CONCLUSIONS

1.1 INTRODUCTION

Section 109(d)(1) of the Clean Air Act, added by the 1977 amendments, requires that EPA thoroughly review each 5 years the criteria for those pollutants listed under Section 108 and regulated by National Ambient Air Quality Standards (NAAQS) under Section 109. According to this requirement, the first such review of the criteria and standards for hydrocarbons must be completed by December 31, 1980. Most reviews of the criteria for regulated pollutants have led to revisions of the existing criteria documents. In the revision process, thorough evaluation is made of comprehensive scientific information that will form the basis for a decision on the need for and nature of any revisions to the National Ambient Air Quality Standard (NAAQS) for the pollutant under consideration. As EPA proceeded in its review of information on hydrocarbons, it became apparent that revisions to the original criteria document were not appropriate. Rather, EPA's review indicated that the unique nature of the criteria and standards for hydrocarbons made the usefulness of revising the original criteria document questionable, and indicated instead that a sufficient basis for regulatory decisions relative to the hydrocarbon standard could be established by means of a thorough review of current scientific data followed by the identification of certain key facts, or pivotal criteria, for hydrocarbons. Chapter 4 presents the rationale behind preparation of this document and use of this approach in developing current criteria for hydrocarbons.

The title of the external review draft of this document (February 1980) was not fully descriptive, since both that draft and this document develop and present those criteria pertinent to a review of the NAAQS for hydrocarbons. The present document statisfies the requirements for the review of criteria specified in Section 109(d)(1) of the Clean Air Act. It should be noted that the Clean Air Act does not specify the form in which such reviews should be published or the form in which resulting criteria should be issued.

The 1970 air quality criteria document covered only those organic compounds that are composed solely of carbon and hydrogen and that occur in the atmosphere in the vapor phase. These compounds, hundreds of which have been identified as being emitted into the atmosphere, are collectively referred to as hydrocarbons. Hydrocarbons are a specific class of organic compounds, so that all hydrocarbons are organic compounds but not all organic compounds are hydrocarbons. The 1970 criteria document excluded compounds such as substituted or derivatized hydrocarbons, e.g., halogenated hydrocarbons. It also excluded all organic compounds, hydrocarbon or nonhydrocarbon, that occur in the atmosphere in aerosol or particulate form. It included a brief treatment of aldehydes to ensure coverage of this class of secondary pollutants formed from hydrocarbons in the atmosphere. It should be noted, however, that no standard was subsequently promulgated for aldehydes and that the EPA reference method for hydrocarbons does not measure aldehydes.

Similarly, this issue paper covers only volatile hydrocarbons as defined in the 1970 criteria document and, thus, as covered by the 1971 NAAQS for hydrocarbons. Aldehydes are generally excluded from this paper since they are not hydrocarbons, since they are not covered by the NAAQS for hydrocarbons, and since the 1978 criteria document for ozone and other photochemical oxidants included information on the photochemistry and health effects of aldehydes. Furthermore, the National Academy of Sciences is presently conducting a review of the atmospheric chemistry and effects of aldehyde air pollutants for EPA. In addition, EPA is conducting a thorough review of the health-related data on formaldehyde. At the conclusion of the NAS review, EPA will determine whether further assessment should be conducted as a basis for possible regulatory action on aldehydes. The present EPA assessment of formaldehyde will determine whether health-related regulatory action should be pursued for this specific aldehyde. Also, EPA is currently preparing separate documents that assess the health effects of a number of nonhydrocarbon volatile organic compounds, e.g., perchloroethylene, trichloroethylene, ethylene dichloride, acrylonitrile, and vinylidene chloride.

1.2 BACKGROUND INFORMATION

The class of compounds known as hydrocarbons is unique among the seven pollutants or classes of pollutants listed under Section 108 and regulated under Section 109 of the Clean Air Act. All pollutants regulated by NAAQS except for hydrocarbons are thought to have direct deleterious effects on public health, and, in some instances, on public welfare as well. The criteria developed in 1970 for hydrocarbons showed clearly, however, that hydrocarbons do not directly produce deleterious effects on public health or welfare. Instead, the criteria showed that hydrocarbons indirectly cause adverse health and welfare effects through their contribution to the formation of photochemical oxidants in general and of ozone in particular. Thus, hydrocarbons were the only pollutant or pollutant class regulated under Section 109 solely for the purpose of controlling their secondary atmospheric products.

This approach resulted in an NAAQS that is unique among the seven existing NAAQS in the following respects: (1) it was not based on the health or welfare effects of hydrocarbons, either singly or as a class; (2) it was accompanied by a measurement method that is not as specific for the regulated pollutant as the methods available for other criteria pollutants; (3) it was intended to serve solely as a guide in helping States determine hydrocarbon emission reductions needed to attain the 1971 oxidant standard; and (4) it was not intended to be an enforceable standard having the same regulatory weight and function as the other standards. Because of its intended use as a guideline, it has not been enforced, no State Implementation Plans for its attainment have been required, and no routine monitoring of ambient air levels of nonmethane hydrocarbons has been required under the hydrocarbon standard. In keeping with its use in achieving the oxidant standard (which is now a standard for ozone), the level selected for the 1971 NAAQS for hydrocarbons was fixed in relation to the level selected for the oxidant standard, this relationship having been determined through the application of an empirical model derived from aerometric data in conjunction with the atmospheric dispersion-related equation used in the linear rollback model.

The basis for the existing NAAQS for hydrocarbons, then, is the role of hydrocarbons, along with other volatile organic compounds, as precursors to ozone and other photochemical oxidants. From the review of current scientific information on hydrocarbons that EPA conducted to prepare this document, two facts were established, one qualitative and one quantitative, concerning the basis for the existing hydrocarbon NAAQS:

1. According to present knowledge, vapor-phase hydrocarbons--as a class--contribute to the formation of ozone and other photochemical oxidants in the ambient air.
2. According to present knowledge, no fixed level of nonmethane hydrocarbons can be used nationwide to ensure the attainment and maintenance of the ozone standard.

The first of these facts was clearly established by the 1970 criteria document and confirmed when the criteria for ozone and other photochemical oxidants were revised in 1978. The concept embodied in the second fact above is whether the quantitative relationship between ozone concentrations in ambient air and hydrocarbon concentrations in ambient air is fixed and constant so that an NAAQS for hydrocarbons can be set in relation to the ozone NAAQS. While the concept itself was not explicity addressed in the 1978 ozone criteria document, it was implicit in that document and in the promulgation by the Administrator of EPA in 1979 of an ozone standard without the concomitant revision of the hydrocarbon standard. This more general concept relative to the quantitative aspect of the basis of the current standard is addressed in this document. The replacement by EPA in 1979 of the Appendix J model by other models clearly established the deficiencies of the specific method used in 1970 to quantify the relationship between precursor hydrocarbons and ozone and other photochemical oxidants.

The review of literature undertaken in preparation of this document revealed no evidence that would alter the findings of the ozone document relative to oxidant-precursor relationships. This document fully corroborates that the qualitative aspect of the basis for the NAAQS for hydrocarbons remains valid. Hydrocarbons in ambient air are major precursors to ozone and other photochemical oxidants in ambient air and must be controlled in order to reduce ambient air levels of ozone and othe photochemical oxidants. However, the quantitative aspect of the basis of the present NAAQS for hydrocarbons was not substantiated in the 1978 ozone criteria document, a finding that is also fully corroborated by this document.

The two basic facts cited above, which are discussed in Sections 5 and 6, are key criteria required for regulatory analyses and decisions regarding the basis for the current hydrocarbon NAAQS. However, no review of criteria for hydrocarbons could be considered complete without the inclusion of the answer to a crucial question relating to the possible need for a hydrocarbon class standard on a new basis. That question is:

3. According to present knowledge, do vapor-phase hydrocarbons--as a class--cause adverse effects on public health or welfare at or near levels found in the ambient air?

The answer to this question provides the third key criterion needed for a regulatory decision relative to an NAAQS governing hydrocarbons as a class. The data base from 1970 to the present has been thoroughly reviewed to ascertain the answer to this crucial question.

The following additional questions, pertinent but subsidiary, are also addressed, using the same data base:

4. What analytical methods are available for ambient air hydrocarbons? How accurate and specific are they?
5. What is the relationship between measurements of hydrocarbon mass in the ambient air and consequent oxidant pollution? That is, do monitoring methods for hydrocarbons reflect the oxidant-forming potential of hydrocarbon mixtures in the ambient air?
6. What are the major sources of hydrocarbon emissions to the atmosphere?
7. What kinds of hydrocarbons are emitted from these sources?
8. What are the levels of emissions from the major sources?
9. What are the ambient air levels of hydrocarbons as a class and of certain individual hydrocarbons or subclasses of hydrocarbons?
10. Have any subclasses of vapor-phase hydrocarbons (aliphatics, alicyclics, aromatics, or mixtures) been demonstrated to have adverse health or welfare effects--as a subclass? If so, what kind and at what levels?

11. Have any individual hydrocarbons been shown to have adverse health or welfare effects? If so, what kind and at what levels?

The answers to these questions have been presented in this document (Chapters 5 and 6) because of their bearing on the three key criteria addressed.

Ambient air data in the form of concentrations of total nonmethane hydrocarbons; of total paraffins, olefins, and aromatics; and of individual species of hydrocarbons have been presented mainly for contrast with the levels reported in the health and welfare effects sections. EPA must be able to relate health and welfare effects data with data on the levels and composition of atmospheric burdens of hydrocarbons.

In order to assess properly the validity and relevance of the ambient air data, at least some information has to be presented on measurement methodology, since any errors or problems in methodology must be taken into account when relating ambient air data to effects information. Thus, a review of the basic measurement methods and the relative merits of those methods has been presented.

A fairly lengthy section on sources and emissions of hydrocarbons, including some nonhydrocarbon organic compounds, has been included in this issue paper. It is helpful for the EPA regulatory office to have a summary of sources and their emissions and to be aware of possible trends in technology that could result in changes in the composition or levels of ambient air hydrocarbons. Fuel conversion in stationary combustion sources, changes in auto emission controls, possible fuel conversion for mobile sources, or an increase in the proportion of diesel vehicles in operation are examples of the kind of technologic changes that would influence the composition or levels of hydrocarbons emitted. Consequently, a review of what is presently known on sources, levels, and kinds of emissions of hydrocarbons has been presented in this document.

Health effects information has been presented according to subclasses of hydrocarbons to permit identification of any associations between compound subclass and any possible adverse health effects.

The sections that follow summarize the information given in the body of this report and are presented in accordance with the organization of Chapters 5 and 6.

1.3 CONTRIBUTION OF HYDROCARBONS TO OXIDANT FORMATION

The information presented in Sections 5.1 and 6.1 substantiates that most, if not all, vapor-phase hydrocarbons participate in a complex series of photochemical reactions that give rise to the formation of ozone and other photochemical oxidants in ambient air. Hydrocarbons are involved in the formation of ozone and other photochemical oxidants through the generation, from hydrocarbons, of alkylperoxy and hydroperoxy radicals that react with nitric oxide to form nitrogen dioxide (NO_2). The increase in production of NO_2 brought about by the radicals generated from hydrocarbon oxidation results in a greater abundance of atomic oxygen that subsequently reacts with molecular oxygen, in the presence of a third body, to form ozone (Sections 5.1 and 6.1).

Evidence accumulated from both experimental and theoretical research over the past decade strongly supports the position that reducing the emissions of hydrocarbons will reduce ambient air concentrations of ozone. Research results continue to indicate, however, that the hydrocarbon-ozone relationship is exceedingly complex and that it is dependent upon many factors, including the ratio of nonmethane hydrocarbons to nitrogen oxides. Research has increasingly corroborated over the past decade that volatile organic compounds other than hydrocarbons are also photochemically reactive in the production of ozone and other photochemical oxidants. The first fact corroborated in this document is that vapor-phase hydrocarbons, along with other compounds, do indeed serve as precursors to ozone and other photochemical oxidants in the ambient air.

Hydrocarbons are also precursors to other secondary products of atmospheric reactions, namely, aerosols and acid precipitation.

Evidence to date indicates that unsaturated hydrocarbons, specifically alkadienes and cyclic alkenes, are important precursors to secondary aerosols (aerosols formed in the atmosphere and not emitted as aerosols). Data show, however, that only a small fraction of the vapor-phase hydrocarbons in ambient air is converted into particulate matter. Though specific hydrocarbons differ in their capacity to form aerosols (Section 6.5), control of hydrocarbons for the sake of ozone/oxidant control will suppress the ambient air levels of those specific hydrocarbons leading to the formation of secondary aerosols.

Hydrocarbons participate in the acidification of rain through their role as precursors to hydroperoxy radicals ($HO_2^{\cdot}$) and, thus, hydrogen peroxide, which under certain atmospheric conditions oxidizes sulfur dioxide to sulfur trioxide. In the presence of moisture in the atmosphere, sulfur trioxide forms sulfuric acid.

1.4 MEASUREMENT METHODOLOGY

Routine measurements of total and nonmethane hydrocarbons in ambient air are made using continuous monitoring analyzers that employ a flame-ionization detector (FID) as the sensing element. This method is the EPA-adopted method promulgated when the 1971 NAAQS for HC was promulgated. Nonmethane hydrocarbon concentrations are determined by separating methane chromatographically from the remaining hydrocarbons in the ambient air sample and determining the methane concentration separately. Subtraction of the value for methane yields the nonmethane hydrocarbon concentration. The methane concentration is of no particular interest since methane is photochemically nonreactive.

The FID is sensitive to a fraction of a part-per-million (ppm) carbon, expressed as methane. The FID is not specific for hydrocarbons alone but responds to any C-H or C-C bonds. Thus, though it is often referred to as a nonmethane hydrocarbon (NMHC) method, the FID method is more appropriately called a nonmethane organic compound (NMOC) method. The values obtained by this method are a measurement of the mass of the hydrocarbons in ambient air, expressed as ppm carbon or as micrograms of carbon per cubic meter ($\mu g/m^3$). The values give no indication of the kind of hydrocarbons measured or the mole concentration of total hydrocarbons measured.

A collaborative study in 1974 by 16 different users of the EPA reference method (FID) showed that at the level of the NAAQS for HC, 160 $\mu g/m^3$ (0.24 ppm) C, the majority of the measurements were in error by 50 to 100 percent, with no consistent bias. At higher hydrocarbon concentrations, the measurement error was considerably less, only 0 to 20 percent.

Gas chromatography (GC) is a more specific method than the FID analyzer and is the only method available for measurement of individual hydrocarbons. It is more specific because individual compounds can be identified and peaks resulting from the presence of organic compounds other than hydrocarbons can be excluded from the determination of total nonmethane hydrocarbons. GC techniques are sensitive to the part-per-billion (ppb) level. GC techniques are more sophisticated and time-consuming, however, than the FID analyzer and do not lend themselves to continuous monitoring or to long-term analysis of hydrocarbons in ambient air.

1.5 SOURCES AND EMISSIONS

As noted in the preceding section (1.4), FID measurement methods are not specific for hydrocarbons but may give a positive response to the presence of many other organic compounds, even though that response may be a reduced response. Also, as noted in Section 1.3, many volatile organic compounds besides hydrocarbons participate in the atmospheric photochemical reactions that give rise to ozone and other photochemical oxidants. The Environmental Protection Agency in recent years has for these reasons included hydrocarbon source and emissions data under the broader category of volatile organic compounds (VOC).

Volatile organic compounds are emitted from both natural and manmade sources. Methane emissions from natural sources in the United States have been estimated at about 4.5×10^7 metric tons/year (5×10^7 tons/year). Though its role in photochemical smog formation is under renewed investigation, evidence to date indicates that methane plays no significant role in the photochemical formation of oxidants and other smog components. Emissions of isoprene and terpenes from vegetation in the United States have been estimated to be about 6.4×10^7 metric tons/year. Isoprene and terpene emission densities are not temporally or spatially uniform in the United States. Rather, about 43 percent of such emissions occur in the summer months and about 45 percent of the annual isoprene and terpene emissions occur in the Southern United States. The role of natural (vegetational) hydrocarbons in the formation of ozone is controversial at present. Detailed discussions of this controversy are not included in this document but are available in the open literature. The issues in question were addressed in the 1978 criteria document for ozone and will again be treated when that document is revised again.

On a nationwide basis, manmade emissions of volatile organic compounds from all sources were estimated to be 28.3×10^6 metric tons/year in 1977, a decrease of about 3 percent since 1970. In 1977, the major source of volatile organic emissions was transportation (41 percent), followed by industrial processes (36 percent), and miscellaneous organic solvent use (3.7 percent). Emissions due to evaporative losses and industrial processes increased from 1970 through 1977, but emissions from highway vehicles decreased by about 7 percent over the same period as a result of the use of control devices. The decrease in vehicle emissions occurred in spite of an estimated 30 percent increase in motor vehicle miles traveled during that period and reflect intensive effort on the part of the auto industry to reduce hydrocarbon and other pollutant emissions from autos and other highway vehicles.

Within the categories of industrial processes and miscellaneous sources of VOC emissions, chemical manufacturing, industrial solvent use, and miscellaneous solvent use (domestic and commercial) together resulted in VOC emissions of about 9.1×10^6 metric tons in 1977, nearly the total of VOC emissions produced by highway vehicles (9.9×10^6 metric/tons year). As stated earlier, hydrocarbons are just one class of those compounds categorized by EPA as volatile organic compounds. A rough estimate of the percentage of VOC emissions that are actually hydrocarbon emissions may be obtained by assuming that emissions from chemical manufacturing and from industrial and miscellaneous organic solvent use are 100 percent non-hydrocarbon VOC. While this assumption is not wholly accurate, it is also true that exceptions to it are more than likely offset by non-hydrocarbon VOC emissions such as oxygenated or even halogenated hydrocarbons from highway vehicles, stationary source fuel combustion, oil and gas production and marketing, and miscellaneous combustion sources. Given the basic assumption, non-hydrocarbon emissions may represent as much as 32 percent of the total VOC emissions estimated for 1977 (9.1×10^6 MT/yr out of 28.3×10^6 MT/yr).

1.6 AMBIENT AIR CONCENTRATIONS

The monitoring of hydrocarbons that is conducted by the states is for the purpose of determining reductions in HC emissions needed to control oxidant levels and is not required for the purpose of enforcing the HC NAAQS. Hydrocarbon monitoring by the states is conducted mainly to obtain ambient air data that can be used as input to the respective models used to determine the percentage reductions in HC emissions that are needed to attain and maintain the NAAQS for ozone.

Since routine monitoring has not been required, most of the data available have been obtained from field studies conducted by EPA. Data presented in this document were obtained from these field studies as well as from the open literature. Ambient air data are generally reported as parts per million or parts per billion carbon (ppm or ppb C), whereas data reported by physicians and toxicologists in animal and human exposure studies are generally expressed as ppm or ppb compound.

In a recent compendium of ambient air data on gas-phase hydrocarbons by Graedel (Section 6.4), the detection of over 1000 organic compounds is documented according to class of hydrocarbon and source. The most abundant hydrocarbon by far is methane, with a concentration range of 1.3 to 4 ppm; ethylene and acetylene are second and third, respectively, with concentrations in the ppb range. The most abundant of the alkanes are ethane, propane, butane, pentane, and isopentane, with upper limits all above 50 ppb but less than 200 ppb. The most abundant unsaturated alkenes and alkynes are ethylene and acetylene, which are typically present at concentrations less than about 50 ppb but have been detected at concentrations as high as 227 to 700 ppb. In comparison to all the other hydrocarbon classes, the alicyclic compounds are very limited in number and their combined concentrations are quite low. Excluding benzene, toluene, and the xylenes, the upper limit of the concentrations of individual aromatics is less than 22 ppb. Benzene concentrations range from 0.025 to 57 ppb; toluene ranges from 0.005 to 129 ppb; and the xylenes range from 0.5 to 61 ppb.

Many of the published detailed studies of organic compounds in the urban atmosphere were conducted in the 1960s. Results of those studies were summarized and discussed in the 1970 criteria document for hydrocarbons. Published data on total NMHC levels in urban atmosphere from 1970 through the present are relatively abundant, but most of these data suffer from considerable measurement error since they were obtained with FID instrumentation. Data obtained by EPA with gas chromatography, as well as FID, in field studies in St. Louis and Houston are representative of urban atmospheres; however, the atmospheric hydrocarbon burdens of these two cities are influenced by different sources. St. Louis is dominated by automotive-related sources whereas Houston is influenced by both automotive and industrial emissions. Data reported in this document for the greater Boston area are representative of HC concentrations found in suburban areas and data reported for Wilmington, Ohio, are representative of levels found in rural areas. The Houston area has a greater number of hydrocarbon-polluting industries than St. Louis or the Boston area (suburban sites), and certainly more than the rural area represented by Wilmington, Ohio, even though local influences there include a refinery.

In general, the individual hydrocarbon concentrations observed in the field studies conducted by EPA were less than the upper limits quoted by Graedel (Section 6.4), though in a few cases the values were higher. Typical concentrations of total nonmethane hydrocarbons (EPA studies) in urban atmospheres are in the range of 0.1 to 3 ppm C. Concentrations of total nonmethane hydrocarbons in rural areas range from 0.04 to 0.2 ppm C.

As the data presented in Section 6.4 show, natural hydrocarbons are not detected in ambient air in urban areas nor even at most sites outside of forest canopies in rural areas. Data given in Sections 6.3 and 6.4 show that concentrations of natural hydrocarbons fall off rapidly with distance from the vegetation that emits them. Measurements by Westberg, for example, show no detectable levels of natural hydrocarbons outside the forest canopy, whereas levels of hydrocarbons associated with manmade sources (benzene and toluene) are virtually the same within and outside the canopy (Section 6.4). Westberg reported average natural hydrocarbon concentrations of 0.2 ppb C in air sampled within an Idaho conifer forest. At rural sites in the east, terpene concentrations of 0.5 to 2 ppb C and isoprene concentrations of about 2 ppb C have been reported, with total NMHC concentrations of about 100 ppb C at these sites. Other measurements, made at various rural and remote areas in the southeast, show ambient air concentrations of total natural hydrocarbons (isoprene and/or terpenes) to range from $\leq$ 4 to 10 ppb C, with total NMHC averaging 40 to 100 ppb C. All of the measurements showing detectable levels of natural hydrocarbons in rural and remote areas have been made within canopies or very short distances from forests or large stands of trees. In Wilmington, Ohio, measurements made at a site in an open field showed no detectable levels of natural hydrocarbons.

1.7 HYDROCARBON/OXIDANT RELATIONSHIP

The qualitative aspects of hydrocarbon-oxidant relationships are better understood now than in 1970 when the hydrocarbon criteria document was published. Factors affecting the atmospheric photochemical processes were treated in detail in the 1978 criteria document for ozone and other photochemical oxidants. That document also gave in detail other qualitative and quantitative information on the precursor-oxidant relationship, including information on the photochemical products to be expected from specific organic precursors and the reaction rates, where known, for the formation of those products. Such information has therefore been discussed only briefly in this paper. Among those physical factors having important, even profound, influence on the photochemical formation of ozone and other photochemical oxidants are: temperature, sunlight intensity, spectral distribution of sunlight, occurrence and persistence of inversions, and other meteorologic, geographic, or climatologic factors. Among the chemical factors that are important influences are the initial precursor concentrations (including background levels); composition of the NMHC mix in ambient air and the relative reactivities of the species present; and the NMHC/NO_x ratio. (In this context, NMHC actually refers to nonmethane organic compounds, NMOC.) Data on precursor-oxidant relationships, including both theoretical and empirical data, corroborate that a reduction in NMOC will result in reductions in ambient air concentrations of ozone and other photochemical oxidants. Available reactivity data indicate that all hydrocarbons that participate in the formation of peroxyacyl nitrates also participate in the formation of ozone, even though reactivities of the various hydrocarbons may differ with respect to the different oxidant products.

It is with respect to quantifying the precursor-oxidant relationship that the relative disparity between the 1970 and 1979 data bases becomes apparent. The term "relative disparity" is used here because the Administrator acknowledged in the 1970 criteria document and in the notice of promulgation of the 1971 standard the limitations of models available then for describing the relationship between hydrocarbons and oxidants. The Appendix J model was the best one available in 1970 when the air quality criteria document was written; and in using it in its 1971 standard-setting process, EPA made the most effective use it could of available data describing the hydrocarbon-oxidant relationship. An attempt has been made in Sections 5 and 6 of this paper to note key characteristics and shortcomings of the Appendix J method for determining reductions in hydrocarbon emissions needed to achieve the 1971 NAAQS for oxidant. It must be emphasized, however, that EPA has since replaced this method by the promulgation of other models because data obtained since 1970 have substantiated the theoretical inadequacies of the Appendix J method.

The characteristics of newer models (AQSM and EKMA) for determining necessary reductions in hydrocarbon emissions have been briefly summarized in Section 6. It is apparent that the models give different results, as stated by EPA when it promulgated the 1979 NAAQS for ozone. It is also apparent that no one model can serve all localities. EPA is engaged in a continuing process of issuing additional information on precursor/oxidant models to the states to be used in preparing revisions to State Implementation Plans.

No model is available that can quantify the relationship between HC emissions and ozone across the entire nation. The relationship between HC precursor emissions and oxidant air quality is such that the attainment and maintenance of a nationally applied ozone standard depend upon HC emission reductions specifically tailored in accordance with the HC mix (profile), HC levels, NO_x levels, HC/NO_x ratio, and meteorological parameters of local or, at most, regional areas. The most fundamental and sophisticated of the models, the photochemical diffusion models (air quality simulation models, AQSM), relate hydrocarbon emissions directly to ozone air quality by means of chemical reaction mechanisms coupled with meteorological factors. These AQSMs require meteorological and emissions data, disaggregated spatially and temporally, for the specific area or region in which ozone levels are to be controlled.

Irrespective of which of the EPA-prescribed models may be used, however, an important point to be made is that all of the models are used to determine needed reductions in hydrocarbon emissions rather than reductions in ambient air levels of hydrocarbons as a means of achieving the ozone standard. To link ozone concentrations to a fixed hydrocarbon concentration in air nationwide would not be consonant with what is now known about the atmospheric reactions and processes that result in the formation of ozone, many of which are dependent upon meteorological and source characteristics that are by nature local, or perhaps regional, but not national. Thus, according to present knowledge, the relationship between hydrocarbon precursors and resulting ambient air levels of ozone and other oxidants is not uniform or monotonic across the nation and cannot be described on a nationwide basis. Rather, it can be quantified with any degree of accuracy only on a local, area-specific basis. The scientific evidence accumulated since 1971 has invalidated the concept that any one ambient air level of hydrocarbons can be derived that describes nationwide the relationship between hydrocarbon emissions and resulting ozone/oxidant ambient air levels or that in any way numerically controls ambient air levels of ozone/oxidant nationwide.

1.8 HEALTH AND WELFARE EFFECTS OF HYDROCARBONS

The criteria developed by EPA in 1970 for hydrocarbons provided no health data directly related to ambient levels of gaseous or volatile hydrocarbons as a pollutant class. The only direct adverse effect attributable at that time to gas-phase hydrocarbons at levels approximating ambient air concentrations was the vegetation damage from ethylene; however, this effect was limited to certain species of plants and certain areas of the country and was by no means a problem nationwide. The sole purpose of prescribing a nonmethane hydrocarbon standard was to control the ambient levels of specific smog components such that the oxidant standard would be met.

Since the original data base was developed, the criteria document published, and the standards promulgated for hydrocarbons, nearly 10 years have passed. A review of the literature since 1970 reveals once again that hydrocarbons, as a class, do not present a significant potential for adverse health or welfare effects at the present detectable levels but that hydrocarbons should be controlled or restricted on the basis of their contribution to photochemical smog and the resultant health and welfare effects of the smog products.

In order for any direct effects on health to be observed from exposure to hydrocarbons, as a class, in the ambient air, the present levels of vapor-phase hydrocarbons would have to be increased by hundreds to thousand of times. One member of this class, however, is present in ambient air at levels that represent a potential for adverse health effects.

This compound, benzene, is a unique aromatic hydrocarbon, and has been implicated in three pathological conditions; namely, leukemia, pancytopenia, and chromosomal aberrations. The concern over benzene as a leukemogen and as the cause of other severe systemic toxicities at low exposure levels has been widely recognized, as evidenced by the facts that EPA has listed it as a hazardous pollutant under Section 112 of the Clean Air Act, that NIOSH recently recommended a much more stringent standard for occupational exposure, and that Runion (Section 6) has reexamined the practical impact of such a benzene standard in relation to gasoline exposure as expressed by TLV values. The proposed OSHA standard for benzene that was based on the NIOSH recommendation, however, has recently been overturned by the Supreme Court, based partly on the absence of cost/benefit analysis in the formulation of the standard.

The leukemogenic nature of benzene is specific to the structure of this aromatic hydrocarbon. The insertion of an alkyl substituent into the benzene nucleus to give, e.g., methyl benzene (toluene), completely changes the route by which the substituted compound is metabolized and changes the resulting chronic toxicity to the point that toluene lacks the potential to cause hematological damage. The toxicity of the xylenes is even greater than that of benzene or toluene in acute exposures, but less than that of benzene and toluene in chronic exposures.

Relative to benzene, the remaining hydrocarbons, whether they occur as mixtures (Carpenter's solvents, Section 6.6) or as individual hydrocarbons, can in general be tolerated at elevated concentration levels. In the case of the aliphatic hydrocarbons, no threshold limit values have been assigned to the collective class of hydrocarbons known as the "simple asphyxiants" since their tolerable concentrations in air are limited only by the percentage (18 percent) of available oxygen. Until recently, the C_5-C_8 alkanes were considered innocuous as evidenced by TLV's of 500 ppm or more; however, NIOSH has now recommended that a TLV limit of 350 mg/m^3 be established for total C_5-C_8 alkanes--which includes pentane, hexane, heptane, and octane--based upon chronic neurological disorders. On a volume-to-volume basis, these concentrations are equal to about 120 ppm pentane, 100 ppm hexane, 85 ppm heptane, and 75 ppm octane. No studies suggest that any of the gas-phase aliphatics are carcinogenic, mutagenic, or teratogenic in humans or experimental animals; nor is there any reason to suspect that they will be found to produce such effects based on their chemical structures relative to known compounds that exhibit these effects. Alkanes and alkenes, based on limited bioassay data, have been classified as noncarcinogenic; however, some of the long-chain (C_{12} or greater) aliphatic hydrocarbons have been implicated as cocarcinogens or tumor promoters, based on mouse skin experiments. These long-chain aliphatics are not generally emitted as gases and are not generally encountered in the atmosphere in the gas phase.

Toxicologically, the alicyclic compounds, as a class, resemble the previously discussed aliphatic hydrocarbons, in that they act as general anesthetics and central nervous system depressants with a relatively low order of acute toxicity. No occupational or epidemiological evidence was found to indicate that naphthenes (alicyclic components of gasoline and other hydrocarbon mixtures) give rise to systemic effects nor are they implicated as hematopoietic toxicants. Unlike the aliphatic hydrocarbons, the degree of toxicity of the alicyclic hydrocarbons does not correlate with structural characteristics. Naphthene vapors at high concentrations cause irritation of the mucous membranes, with the saturated hydrocarbons generally causing less irritation than the corresponding unsaturated. No studies were found regarding the carcinogenic, mutagenic, or teratogenic potential of any alicyclic hydrocarbons.

Studies by Carpenter (Section 6.6) on miscellaneous hydrocarbon mixtures lend additional support to the concept that the majority of aliphatic and aromatic hydrocarbons, with the exception of benzene, appear to be relatively nontoxic, even when encountered as mixtures. The lowest suggested hygienic standard for these solvent mixtures was 90 ppm based upon inhalation studies with animals in a lethal atmosphere and based upon the sensory response of human subjects. (As Section 6.6 shows, typical concentrations of total nonmethane hydrocarbons in urban atmospheres are in the range of 0.1 to 3 ppm C. Concentrations in rural areas range from 0.04 to 0.2 ppm C.)

No welfare effects are produced by hydrocarbons as a class at or near ambient levels. The effects of a specific hydrocarbon, ethylene, on vegetation have been well documented. In specific areas of the country, due to a combination of meteorological conditions and vehicle exhaust emissions, the levels of ethylene in the ambient air have resulted in damage to ornamental plant species. However, ethylene does not appear to be a problem nationwide, partly because the susceptible ornamentals are grown only in certain localities. Furthermore, the use of catalytic converters on autos, especially improved ones expected in the future, may alleviate the problem, if not eliminate it. Now, as in 1970, there are certain areas of the country that have air standards for dealing with local problems from ethylene. California has an air quality standard for ethylene, for example, which was adopted in 1962 prior to the promulgation of the air quality standard addressing hydrocarbons.

The deleterious effects on public welfare of acid precipitation, to which hydrocarbons are precursors via the formation of hydroperoxy radicals that oxidize SO_2 to sulfur trioxide, have been documented in recent EPA publications and are only briefly summarized in this document (Section 6.7).

In summary, with the exception of benzene hydrocarbons do not appear to cause direct adverse health effects and except for ethylene, no direct adverse welfare effects.

The majority of studies used to support the present health effects position on hydrocarbons are studies of acute exposures. Thus, it may be advantageous to encourage additional research studies under conditions of chronic exposure to low levels of individual hydrocarbons and mixtures to ensure against any long-term effects that are not obvious under acute exposure conditions. As more information develops in the future, the health and welfare effects of individual hydrocarbons may have to be determined and documented in separate assessment reports.

In conclusion, there is no scientific evidence to indicate the need for preparing a more detailed document on hydrocarbons, since now, as in 1970, an air quality standard for hydrocarbons cannot be supported based on the health and welfare effects of hydrocarbons as a class.

2. RECOMMENDATIONS

Based upon its review of the literature and the scientific evidence accumulated, ECAO recommends that the appropriate offices and laboratories of EPA do the following:

1. Make a regulatory decision on the national ambient air quality standard for hydrocarbons, without further documentation on hydrocarbons. In the future, address hydrocarbons as precursors to photochemical oxidants in the ozone/oxidant criteria document.
2. Study and document the effects of ethylene on plants, but as a low-priority item. The effects of ethylene on plants are nonspecific and resemble the effects of certain other pollutants, of other environmental factors, and of some plant diseases. Since gasoline-powered vehicles are its primary source, ethylene is a ubiquitous pollutant. Ethylene damage to plants is not an acute problem nationwide, however, because ethylene-sensitive species--mostly ornamentals--are grown only in certain localities. Also, the use of catalytic converters on autos and other highway vehicles, especially improved converters expected in the future, may alleviate the problem if not eliminate it.
3. Investigate the need for documenting the health effects of aldehydes. Secondary aldehydes formed in the atmosphere from the oxidation of hydrocarbons will be controlled to the extent that hydrocarbon precursors to oxidants are controlled. Aldehydes are also primary pollutants, however, and as such are emitted directly

into the atmosphere from a variety of sources. Some of the aldehydes (e.g., formaldehyde) are photochemically reactive and may also be deleterious to human health. The decision to document the effects of aldehydes should probably wait on the completion by NAS of its document on aldehydes; and should wait on the preparation by EPA of its assessment of formaldehyde, already in progress.

4. Inasmuch as chronic exposure data are lacking, consider initiation by EPA of research on the long-term health effects of low levels of individual hydrocarbons selected on the basis of toxicologic effects coupled with ambient air concentrations. If evidence for adverse health effects accrues from such research or in the open literature, document the health effects of individual hydrocarbons on a case-by-case basis to determine the need for their individual regulation.

5. Available data indicate that volatile organic emissions, including those of hydrocarbons, from some stationary sources, are poorly characterized with respect to the magnitude of emissions and, in some instances, even species. Efforts to identify magnitude and species of HC emissions from stationary sources should be intensified, so that any changes in qualitative profiles of emissions resulting from technologic changes, fuel conversion, etc., can be detected before such changes are pervasive enough to affect profiles of ambient air HC. As species and the magnitude of emissions are identified, study on a continuing basis the need for preparing health assessment documents on individual compounds.

6. Continue development of an accurate and reliable field instrument for measurement of total nonmethane organic compounds (NMOC) in ambient air. Develop instrumentation for source emission measurements of NMOC, possibly including instrumentation for measuring fluxes in organic vapors from evaporation losses. Continue to refine methodology and instrumentation specific for measurements of individual nonmethane hydrocarbons in ambient air.

3. INTRODUCTION

3.1 BASIS FOR AIR QUALITY CRITERIA AND NATIONAL AMBIENT AIR QUALITY STANDARDS

Passage of the Clean Air Act Amendments of 1970 marked the initiation of the present role of the Federal government in air quality management by providing authority for establishing national ambient air quality standards. The 1977 amendments to the Clean Air Act requires the Administrator to publish, and revise from time to time a list that includes each air pollutant--

> (A) emissions of which, in his judgment, cause or contribute to air pollution which may reasonably be anticipated to endanger public health or welfare;
>
> (B) the presence of which in the ambient air results from numerous or diverse mobile or stationary sources; and
>
> (C) for which air quality criteria had not been issued before the date of enactment of the Clean Air Amendments of 1970, but for which he plans to issue air quality criteria under this section.[1]

These amendments further require the Administrator to develop criteria for all pollutants listed. The criteria are to reflect accurately the latest scientific knowledge useful in indicating the kind and extent of all identifiable effects on public health or welfare that result from exposure to each of the pollutants listed. The criteria are to include information on (1) known or anticipated adverse effects of the pollutants on welfare; (2) interactions between the criteria pollutant and other pollutants in the atmosphere if those interactions will result in adverse effects on public health or welfare; and (3) variables, including atmospheric conditions, that may alter the effects of the listed pollutant on public health or welfare. Though criteria have historically been issued in the form of "criteria documents," the Clean Air Act does not specify the form in which criteria must be issued.

Simultaneously with the issuance of criteria, the Administrator is to provide to the States and appropriate air pollution control agencies information on techniques for controlling the criteria pollutant. In addition, the Administrator must simultaneously propose primary and secondary national ambient air quality standards that specify levels of air quality that, based on the criteria issued and according to the Administrator's judgment, should not be exceeded if public health and welfare, respectively, are to be protected. After a suitable period of public comment and review ($\leq$90 days), the Administrator is required to promulgate primary and secondary national air quality standards, with such modifications as he deems appropriate.

3.2 BASIS AND NATURE OF PRESENT REVIEW OF CRITERIA FOR HYDROCARBONS

Section 109(d)(1), added to the Clean Air Act in 1977, requires that EPA review each 5 years, or more often if evidence warrants it, the criteria for those pollutants listed under Section 108 and regulated by National Ambient Air Quality Standards (NAAQS) under Section 109.[1] According to this requirement, the first such review of the criteria and standards for hydrocarbons must be completed by December 31, 1980.

The Environmental Protection Agency (EPA) therefore initiated earlier this year the appropriate literature searches and review procedures, and confirmed early in the review that current data on hydrocarbons do not substantially alter, on two of three major issues, the scientific position on hydrocarbons that prevailed when the first criteria document for hydrocarbons[2] was written in 1970. Furthermore, preliminary review by EPA of the criteria developed in 1970, and of the data base on hydrocarbons compiled since then, called into question the fruitfulness of revising the original criteria document for hydrocarbons. Instead, that review indicated the preferability of preparing a document that would serve as a basis for an appropriate regulatory decision by the Agency by means of a thorough review of current scientific data followed by the identification of certain key facts, or pivotal criteria, for hydrocarbons.

To fulfill its purpose, this document is essentially threefold in nature: (1) it presents those aspects of hydrocarbons and of the NAAQS for hydrocarbons that are unique among the criteria pollutants and the standards regulating them; (2) it presents a brief review of the key criteria developed in 1970 and used in the standard-setting process of 1971; and (3) it examines the 1970-1980 data on hydrocarbons that are pertinent to those key criteria. This document is based on a comprehensive survey of available health and welfare effects information, but the document itself is not intended to be an exhaustive review of all aspects of hydrocarbon pollution. Rather, in areas other than health and welfare effects, an attempt has been made to review those aspects of hydrocarbon pollution pertinent to the criteria developed in 1970 and, relative to those criteria, to present only those established facts that represent a scientific consensus of present knowledge concerning hydrocarbons. The health and welfare effects information presented is the result of a thorough screening of the literature but is given in as concise a form as possible.

A number of issues concerning the role of hydrocarbons in the formation of ozone and other photochemical oxidants are important in the context of formulating and executing effective control strategies for ozone. These issues include the contribution of transported precursors to ozone levels in both urban and rural ambient air; the role of natural hydrocarbons in the formation of ozone in rural areas; and the relative contributions of oxidized hydrocarbons versus their parent compounds in ozone formation. While these are exceedingly important issues with respect to the attainment and maintenance of the ozone standard, they are not germane to the facts and issues concerning the existing hydrocarbon standard. Thus the focus of this document is those criteria needed for regulatory analyses and decisions regarding the hydrocarbon standard itself. Consequently, those issues relating to attainment and maintenance of the ozone standard but not to the necessity for or usefulness of a hydrocarbon standard have been omitted from this document. The air quality management information needed for implementation of the ozone standard was treated in the 1978 ozone criteria document and will be addressed again when the ozone criteria are next revised.

It must be emphasized that the 1970 criteria document for hydrocarbons covered only those organic compounds that are composed solely of carbon and hydrogen and that occur in the atmosphere in the gas phase. It excluded other gas-phase organics such as substituted or derivatized hydrocarbons; e.g., halogenated hydrocarbons. It also excluded all organic compounds, whether hydrocarbon or nonhydrocarbon, that occur in the atmosphere in aerosol or particulate form. It included a brief treatment of aldehydes to ensure coverage of this class of secondary pollutants formed from hydrocarbons in the atmosphere. It did not cover the oxidants, since that class of secondary pollutants formed from hydrocarbons was treated in a separate criteria document for photochemical oxidants.

Similarly, this issue paper covers only gas-phase hydrocarbons as defined in the 1970 criteria document; that is, compounds of carbon and hydrogen ranging in carbon number from 1 to about 12 (C_1 - C_{12}). Aldehydes are treated quite briefly, since the 1978 criteria document for ozone and other photochemical oxidants included information on the photochemistry and health effects of aldehydes.

In addition, the National Academy of Sciences is presently conducting a review of aldehydes for EPA, and EPA is conducting its own assessment of possible health effects of formaldehyde. At the conclusion of these reviews, EPA will determine whether regulatory action on aldehydes should be pursued. Other volatile organic compounds are excluded from this issue paper because they are not hydrocarbons; because they were not covered by the 1970 criteria document or by the 1971 NAAQS for hydrocarbons; and because EPA is currently preparing separate documents that assess the health effects of a number of volatile organic compounds, e.g., perchloroethylene, trichloroethylene, ethylene dichloride, acrylonitrile, and vinylidene chloride.

4. BACKGROUND INFORMATION

4.1 UNIQUE CHARACTERISTICS OF CRITERIA AND STANDARDS FOR HYDROCARBONS

Originally listed as a criteria pollutant pursuant to the Clean Air Act of 1970,[3] hydrocarbons are regulated by a National Ambient Air Quality Standard that specifies that nonmethane hydrocarbons in the ambient air shall not exceed 0.24 ppm C (160 $\mu g/m^3$), maximum 3-hour average concentration (6-to-9 a.m.), more than once per year.[4]

The NAAQS for hydrocarbons is one of six NAAQS promulgated in April 1971 pursuant to Section 109.[4] Of the six NAAQS promulgated in 1971, three governed individual or narrow chemical classes of pollutants--carbon monoxide, nitrogen dioxide, and sulfur oxides; and three governed broad classes of pollutants--photochemical oxidants, total suspended particulates, and gas-phase hydrocarbons. Of the pollutants regulated as classes, hydrocarbons constitute the most diverse and heterogeneous group in terms of (1) their health effects at high occupational levels, (2) the secondary pollutants they give rise to, and (3) the rates at which they react in the atmosphere. Hydrocarbons constitute the largest and most chemically heterogeneous class of pollutants regulated by one standard.

Hydrocarbons are unique among the seven pollutants or classes of pollutants listed under Section 108 and regulated under Section 109 of the Clean Air Act. All pollutants regulated by NAAQS except for hydrocarbons are thought to have direct deleterious effects on public health, and, in some instances, on public welfare as well.[4] The criteria developed in 1970 for hydrocarbons showed clearly, however, that hydrocarbons do not directly produce deleterious effects on public health or welfare.[2] The criteria showed instead that hydrocarbons indirectly cause adverse health and welfare effects through their contribution to the formation of photochemical oxidants in general and of ozone in particular. Thus, hydrocarbons are the only pollutant or pollutant class regulated under Section 109 for the sole purpose of controlling their secondary atmospheric products. Hydrocarbons are the only regulated pollutants that do not produce direct adverse effects in a human receptor but which instead produce direct effects on receptors that are other chemical species in the ambient air. The ambient air may be considered the receptor for which a hydrocarbon dose-response relationship must be determined.

These unique characteristics of hydrocarbons and of the criteria for hydrocarbons have combined to result in an NAAQS for hydrocarbons (HC) that differs from the other NAAQS. The HC NAAQS is unique among the seven existing NAAQS for the principal reasons listed below:

1. The NAAQS for HC was not based upon demonstration of adverse effects of HC on human health or welfare.[4,5]
2. The NAAQS for HC was based solely on the role that HC play in the atmospheric photochemical reactions that produce ozone and other oxidants. HC were regulated in 1971 strictly on the basis that they are precursors to photochemical oxidants.[4,5]
3. The NAAQS for HC was prescribed solely "to provide guidance in formulating emission control strategies for attainment and maintenance of the national standard for photochemical oxidants."[4] It was not intended to be an enforceable standard comparable to the other NAAQS, but was intended to serve as a point of departure to be used

in determining the reductions in HC emissions needed for achievement and maintenance of the oxidant standard (now an ozone standard, since a standard for ozone was promulgated in place of the oxidant standard in February 1979).[6]

All other pollutants or classes of pollutants for which NAAQS exist are regulated on the basis of their direct adverse effects on health or on both health and welfare. Except for hydrocarbons, no other precursor to a regulated pollutant is regulated by its own separate NAAQS.

4.2 NEED FOR A DETAILED CRITERIA DOCUMENT FOR HYDROCARBONS

Air quality criteria are descriptors of the relationship that exists between a pollutant in the ambient air and the effects caused by that pollutant in a specific receptor or receptor population. Criteria, as described by the Clean Air Act,[1] must reflect the latest scientific knowledge available and must identify the effects of a given pollutant expected from the presence of that pollutant in the air. Where possible, criteria are expressed as a dose-response relationship. Since the 1971 NAAQS for hydrocarbons was based on the contribution of hydrocarbons to the formation in ambient air of photochemical oxidants, the dose-response function that was derived was a quantitative relationship between hydrocarbon emissions and the resulting levels of photochemical oxidants formed.

Consequently, the first question asked in EPA's current review of the 1970 criteria and of the 1970 to 1980 data base was whether present knowledge confirms that hydrocarbons in ambient air contribute to or result in the formation of ozone and other photochemical oxidants. The second question asked, as the logical outgrowth of the first, was whether the relationship between precursor hydrocarbons and the resulting oxidant pollution formed was known to be the same as that expressed in the 1970 criteria document and promulgated in 1971, in a different form, as the relationship to be used by the States in attaining and maintaining the oxidant standard. The revision of the air quality criteria for ozone and other photochemical oxidants and the subsequent promulgation in 1979 of the current ozone standard provided answers to both these questions that were confirmed in the present review.[6] Though both these questions are basic and crucial to any regulatory decision on hydrocarbons, they are not sufficient by themselves. The third basic and crucial question that must be asked is whether hydrocarbons, as a class, produce any direct adverse health or welfare effects.

A comprehensive review of all aspects of hydrocarbon pollution in ambient air would be counterproductive since the three questions or issues delineated above are the pivotal issues to be resolved. First, such a review would be precluded on the basis of the volume of information alone, given the number of hydrocarbons that have been detected in ambient air. Second, and most important, there is no known gas-phase hydrocarbon that can serve as a surrogate for the entire class of compounds, as an index of the ambient air level of the entire class, as an index of the oxidant-forming potential of hydrocarbon mixtures in ambient air, or as a control target for the whole class. Consequently, even if a dose-response relationship were derived for a single hydrocarbon, this criterion would be of no value in a review of the existing class standard. It would be useful only for regulatory decisions and action with respect to that individual compound.

In view of these facts, EPA believes that a comprehensive scientific treatise on hydrocarbons is not appropriate as a review of hydrocarbon criteria. This issue paper offers and documents answers to the three basic questions posed above, answers that constitute the pivotal criteria needed to review the NAAQS for hydrocarbons. If review of the standards should prove the scientific answers given to be inadequate, or should raise other key questions that must be answered, EPA will undertake the necessary documentation, either in a revised issue paper or in a more comprehensive document.

5. SUMMARY OF 1970 CRITERIA FOR HYDROCARBONS

This section sets forth in summary form the criteria for hydrocarbons that were published in 1970 and upon which the NAAQS for hydrocarbons promulgated in 1971 was based. This review of the pertinent findings of the 1970 criteria document is presented here to provide background for understanding the basis of the present NAAQS for hydrocarbons and to facilitate comparison of that basis with the current data base on hydrocarbons.

5.1 CONTRIBUTION OF HYDROCARBONS TO FORMATION OF PHOTOCHEMICAL OXIDANTS

As stated in the 1970 document,[2] the ultimate products of the photooxidation of HC in ambient atmospheres would probably be carbon dioxide and water vapor, if a parcel of air were irradiated by sunlight long enough. Complete oxidation of hydrocarbons in an air parcel does not occur, however, because of shortened irradiation time, transport, diffusion, the infusion of "fresh" emissions, etc. At any given time, then, the photooxidation products of hydrocarbons that reside in the ambient air consist of various intermediates in the oxidation process. These intermediates are all capable of further reaction and degradation.

Hydrocarbons become involved in the production of the photochemical air pollution complex not because of their exposure to sunlight, however, but because of their reaction with other components of the atmosphere.[2] The processes by which hydrocarbons participate in the formation of ozone and other photochemical oxidants have been reviewed in detail in two recent EPA documents, Air Quality Criteria for Ozone and Other Photochemical Oxidants (1978),[7] and Air Quality Criteria for Nitrogen Oxides (1979).[8] In addition, the chemistry of oxidant formation and of the role of organic compounds, including hydrocarbons, in those processes has been reviewed in two National Academy of Sciences documents.[9,10] The description given below is a highly simplified version of the complex chemical reactions that actually occur in the atmosphere. It is presented merely to underscore the fact that gas-phase hydrocarbons do contribute to the formation of ozone and other photochemical oxidants.

The photochemical oxidants observed in the atmosphere are ozone (O_3); nitrogen dioxide (NO_2); and peroxyacetyl nitrate (PAN).[9] Several other substances, such as hydrogen peroxide (H_2O_2), may be classified as photochemical oxidants, but their common presence in smog is not well established.[9] Of these oxidants--all of which are secondary pollutants formed as a result of chemical reactions in the atmosphere--ozone occurs in the highest concentrations.

Ozone formation begins with the photodissociation of nitrogen dioxide (NO_2), as shown in Equation (5-1):

$$NO_2 + h\nu \rightarrow O + NO \qquad (5\text{-}1)$$

The oxygen atoms thus formed react with molecular oxygen in the presence of a third body (M):

$$O + O_2 + M \rightarrow O_3 + M \qquad (5\text{-}2)$$

These two reactions together form a mechanism for ozone formation in the atmosphere, a mechanism that is completed by an additional reaction in which NO_2 is regenerated:

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad (5\text{-}3)$$

The role of hydrocarbons in promoting reactions 5-1 through 5-3 is complex, and at the time of the 1970 document was not very well understood. Although of central importance in smog chemistry, reactions (5-1) through (5-3) by themselves do not explain the atmospheric buildup of ozone.[9] If only these three reactions were important, the photodissociation of nitrogen dioxide would rapidly establish a small, steady-state concentration of ozone expressed by the equation:

$$[O_3] = \frac{k_1\,[NO_2]}{k_3\,[NO]} \qquad (5\text{-}4)$$

The photolysis of nitrogen dioxide alone then, does not explain the atmospheric accumulation of ozone, even though it is the mechanism of ozone formation.[9] The dominant factor in this system is the ratio of NO_2 to NO. Once the conversion of NO to NO_2 is explained, the ozone concentration follows the ratio of NO_2 to NO concentrations given in equation (5-4).[9] What was inexplicable until about 1970 was the rapidity of oxidation of NO to NO_2 and the continuing conversion of NO into NO_2 during the buildup of ozone, because this defies the relatively simple theoretical relationship described in equation (5-4).

Early laboratory studies had implicated hydrocarbons, especially olefins, in the formation of ozone by showing that both ozone and ground-state atomic oxygen would attack reactive hydrocarbons. Modeling and smog-chamber simulations have since shown that significant oxidant formation occurs with nitrogen oxides (NO_x) plus aldehydes, or with NO_x plus nonmethane hydrocarbons.[9] Though the mechanism had barely been suggested when the 1970 criteria document was written, it is now known that hydrocarbons--along with the other oxidizable pollutants such as aldehydes and CO--serve the function of regenerating free radicals that react with oxygen in the air to form alkylperoxy and hydroperoxy radicals.[9] These radicals react with NO to form NO_2:

$$HO_2 + NO \rightarrow OH + NO_2 \qquad (5\text{-}5)$$

or

$$RO_2 + NO \rightarrow OH + NO_2$$

Thus, these oxidizable pollutants can be thought of as pumping the nitric oxide to nitrogen dioxide. In the process, hydrocarbons become degraded to other compounds, some of which are also photochemically reactive, such as formaldehyde. The amount of "pumping" that can be done, and thus the amount of oxidant formed, depends in a nonlinear manner on both the reactivity of the oxidizable pollutant--in this case, hydrocarbons--and its concentration.[9] Advances made since 1970 in understanding the reaction mechanisms involved are summarized in Section 6.

5.2 MEASUREMENT METHODOLOGY

As stated in the 1970 air quality criteria document for hydrocarbons, the complexity of the mixtures of hydrocarbons present in ambient air demands sophisticated instrumentation and techniques for measurement. In 1970 a technique was already available for the measurement of the concentration of total hydrocarbons in ambient air. Originally developed as a detector for gas chromatography, this flame ionization technique (FID) was adapted for total hydrocarbon analysis around 1960.[11] In the technique, a sensitive electrometer detects the increase in ion intensity resulting from the introduction into a hydrogen flame of a sample of air containing any organic compound (e.g., hydrocarbons, aldehydes, alcohols). The response is approximately in proportion to the number of organically bound carbon atoms in the sample, but its response to carbon atoms in different compounds is nonlinear. That is, the response of the detector to different classes of hydrocarbons is variable and the response appears to fall off rapidly with increasing carbon number.[12] FID data are usually expressed as the calibration gas used: for example, parts per million (ppm) of carbon as methane. The fact that FID response may be, and often is, related to different reference compounds (methane, propane, butane, etc.) further complicates the comparability, interpretation, and usefulness of FID data.[12] Carbon atoms bound to oxygen, nitrogen, or halogens give reduced or no response; hence, the method may detect oxygenated hydrocarbons such as aldehydes but does not actually measure their concentrations. The instrument responds to hydrocarbon derivatives approximately according to the proportion of carbon atoms bound to carbon or hydrogen. There is no response to nitrogen, carbon monoxide, carbon dioxide, or water vapor; but there is an oxygen effect, which can be minimized by appropriate operating conditions.

The response of the FID is rapid and, with careful calibration, is sensitive to a fraction of a ppm carbon as methane. Variations in FID response to various hydrocarbons and derivatives detract from the comparability and usefulness of FID data.[13] Practically all continuous hydrocarbon analyzers in use in 1970 utilized the flame ionization detector as the sensing element.

The value of the data obtained from measuring total hydrocarbon concentrations is limited. The high background level of naturally occurring methane obscures variations in levels of other hydrocarbon species which, unlike methane, participate in photochemical reactions and are therefore of principal interest. Consequently, methods for measuring methane separately and determining nonmethane hydrocarbons by subtraction of the methane values had been attempted by 1970 and had met with some success.[2] Many of the nonmethane hydrocarbon data obtained prior to 1970 were data obtained by use of a relatively crude carbon absorber to separate out the methane.[12] At the time the NAAQS for hydrocarbons was promulgated, EPA promulgated as the Federal Reference Method an FID method for determining nonmethane hydrocarbons.[5] In the EPA method, which was developed around 1970 and which represented a major improvement over the carbon absorber, the air sample containing methane and carbon monoxide is passed quantitatively through a stripper column to a gas chromatographic column that separates the two gases. The methane is eluted first and is passed unchanged into the FID. (The CO is eluted into a catalytic reduction tube where it is reduced to methane and is subsequently measured by the FID. The CO measurement is not needed in measuring NMHC.) The NMHC concentration is obtained by subtracting the methane value from the total hydrocarbon concentration.[5] The method is applicable to the semicontinuous measurement of hydrocarbons corrected for methane in the ambient air.[5] This method has been incorrectly called a "total hydrocarbon (THC)" measurement method, when in fact the FID also responds to oxygenated compounds such as alcohols and aldehydes having ≥ 2 carbon atoms, as well as to other volatile organic compounds (VOC).[14] Nevertheless, in the absence of a suitable method specific for hydrocarbons, EPA promulgated this method in 1971 as the best available method, and thus the method of choice, for the measurement of total hydrocarbons and of nonmethane hydrocarbons.[2,4]

Other methods available in 1970 for the measurement of hydrocarbons included spectrometric and gas chromatographic techniques. Available spectrometric methods for total and specific analyses were complex and generally insensitive. Gas chromatographic techniques, while providing the requisite sensitivity and specificity for the measurement of individual hydrocarbons,[15,16] required a high degree of operator skill and experience. Furthermore, they were applicable only to short-term analyses because of the time, effort, and skill involved in data reduction.[2]

5.3 SOURCES AND EMISSIONS OF HYDROCARBONS

Hydrocarbons in the ambient air arise from both natural and man-made (technologic) sources. The presence of hydrocarbons from natural sources was established in 1948 with the measurement of background methane concentrations.[17] Although most natural hydrocarbons arise from biological sources, small and highly localized quantities of methane and a few other lower-molecular-weight hydrocarbons are emitted by geothermal areas, coal fields, natural gas and petroleum fields, and natural fires.[2]

Some estimates of natural methane and of terpenes and isoprene from vegetation were available in 1970. Koyama, in 1963, conservatively estimated the worldwide emission of natural methane to be 2.73×10^8 metric tons per year (3×10^8 tons per year.)[18] Worldwide emissions of volatile terpenes and isoprenes from vegetation were estimated in 1965 by Rasmussen and Went at 4.0×10^8 metric tons per year (4.4×10^8 tons per year.)[19] No estimate of natural emissions in the United States alone was given in the 1970 document.[2]

Total nationwide manmade emissions of hydrocarbons and related organic compounds were estimated at 29.1×10^6 metric tons (32×10^6 tons) for 1968, the base year for which emissions data were available for use in the 1970 document. Transportation (mobile sources) accounted for 52 percent of this estimate. Miscellaneous sources, principally solvent evaporation, constituted the second largest category of sources and contributed 27 percent of these emissions. Industrial processes were third, with 14 percent; solid waste disposal was fourth, with 5 percent; and fuel combustion in stationary sources was fifth, with 2 percent.[2]

Local emissions for 22 metropolitan areas, as opposed to total nationwide emissions, were estimated to range from about 0.04 to 1.2 million metric tons per year (about 0.05 to 1.3 million tons per year), depending on the area. Transportation sources accounted for 37 to about 99 percent of local emissions, and process losses--solvent evaporation and industrial processes combined--accounted for 1 to 63 percent. Thus, total hydrocarbon emissions in 1968, the base year used in the 1970 criteria document, originated primarily from the inefficient combustion of volatile fuel in mobile and stationary sources and from the use of hydrocarbons as process raw materials.[20]

Conventional automobiles (gasoline-powered, internal combustion engines) potentially emit gas-phase hydrocarbons from four sources: engine exhaust, crankcase blow-by, carburetor evaporation, and fuel tank evaporation.[2] Positive crankcase ventilation (PCV) systems were introduced in 1963 that virtually eliminated crankcase blow-by emissions.[21] Emissions from the other three sources were not yet controlled to any appreciable extent in 1968, so that uncontrolled conventional automobiles constituted most of the aggregate of passenger cars and other light-duty vehicles at that time.

5.4 AMBIENT AIR CONCENTRATIONS

Methane concentrations were reported in the 1970 document to range generally from about 0.7 to 1.0 mg/m^3 (1.0 to 1.5 ppm), but to occur often at levels as high as 4 mg/m^3 (6 ppm) in populous areas. Yearly averages of monthly maximum 1-hour average total hydrocarbon concentrations, which included methane, ranged from 8 to 17 ppm (as carbon) at stations of the Continuous Air Monitoring Projects (CAMP) network for 1962 through 1967.[2] Few data were available in 1970 for comparing nonmethane hydrocarbon (NMHC) concentrations at various geographic locations.[2] From the data available in 1968 from the CAMP network, 24-hour average NMHC concentrations, averaged over several months, were about 0.5 to 0.8 ppm C in Washington, D.C.; about 0.6 to 1.5 ppm C in Denver; about 0.8 to 1.3 ppm C in St. Louis; and about 0.6 to 1.3 ppm C in Chicago.[22] In urban areas, the ratio of nonmethane hydrocarbons to methane was estimated at 0.6 in Cincinnati and at 1.9 in Los Angeles in 1964. The higher ratio in Los Angeles may have been a reflection of the greater traffic density in that city.[2]

In a series of 200 samples taken in one urban location, average concentrations of the most abundant hydrocarbons were (in ppm as C): methane, 3.22; toluene, 0.37; *n*-butane, 0.26; isopentane, 0.21; ethane, 0.20; benzene, 0.19; *n*-pentane, 0.18; propane, 0.15; and ethylene, 0.12. Among classes of hydrocarbons, alkanes predominated even when methane levels were excluded. They were followed, in order, by aromatics, olefins, acetylene, and alicyclics.

Detailed hydrocarbon data for samples taken in Los Angeles in 1965, as determined by gas chromatography, are shown in Tables 5-1 through 5-3.[23-27] The hydrocarbons that appear on these tables are typically found in most urban areas. The quantitative profiles differ from one urban area to the next; however, the qualitative profiles do not vary widely in urban areas influenced predominantly by automobile emissions. Examination of these qualitative profiles and comparison with whole gasoline and gasoline vapor constituents

TABLE 5-1. SOME HYDROCARBONS IDENTIFIED IN AMBIENT AIR[23-25]

Carbon number	Class	Compound
1	Alkane	Methane
2	Alkane	Ethane
2	Alkene	Ethylene
2	Alkyne	Acetylene
3	Alkane	Propane
3	Alkene	Propylene
3	Alkene	Propadiene
3	Alkyne	Methylacetylene
4	Alkane	Butane
4	Alkane	Isobutane
4	Alkene	1-Butene
4	Alkene	*cis*-2-Butene
4	Alkene	*trans*-2-Butene
4	Alkene	Isobutene
4	Alkene	1,3-Butadiene
5	Alkane	Pentane
5	Alkane	Isopentane
5	Alkene	1-Pentene
5	Alkene	*cis*-2-Pentene
5	Alkene	*trans*-2-Pentene
5	Alkene	2-Methyl-1-butene
5	Alkene	2-Methyl-2-butene
5	Alkene	3-Methyl-1-butene
5	Alkene	2-Methyl-1,3-butadiene
5	Cycloalkane	Cyclopentane
5	Cycloalkene	Cyclopentene
6	Alkane	Hexane
6	Alkane	2-Methylpentane
6	Alkane	3-Methylpentane
6	Alkane	2,2-Dimethylbutane
6	Alkane	2,3-Dimethylbutane
6	Alkene	1-Hexene
6	Alkene	*cis*-2-Hexene
6	Alkene	*trans*-2-Hexene
6	Alkene	*cis*-3-Hexene
6	Alkene	*trans*-3-Hexene
6	Alkene	2-Methyl-1-pentene
6	Alkene	4-Methyl-1-pentene
6	Alkene	4-Methyl-2-pentene
6	Aromatic	Benzene
6	Cycloalkane	Cyclohexane
6	Cycloalkane	Methylcyclopentane
7	Alkane	2-Methylhexane

TABLE 5-1 (continued)

Carbon number	Class	Compound
7	Alkane	3-Methylhexane
7	Alkane	2,3-Dimethylpentane
7	Alkane	2,4-Dimethylpentane
7	Aromatic	Toluene
8	Alkane	2,2,4-Trimethylpentane
8	Aromatic	*o*-Xylene
		m-Xylene
		p-Xylene
9	Aromatic	*m*-Ethyltoluene
		p-Ethyltoluene
		1,2,4-Trimethylbenzene
		1,3,5-Trimethylbenzene
10	Aromatic	*sec*-Butylbenzene

TABLE 5-2. AVERAGE HYDROCARBON COMPOSITION, 218 AMBIENT AIR SAMPLES, LOS ANGELES, 1965[26]

	Concentration	
Compound	ppm	ppm (as carbon)[a]
Methane	3.22	3.22
Ethane	0.098	0.20
Propane	0.049	0.15
Isobutane	0.013	0.05
n-Butane	0.064	0.26
Isopentane	0.043	0.21
n-Pentane	0.035	0.18
2,2-Dimethylbutane	0.0012	0.01
2-Methylpentane		
2,3-Dimethylbutane	0.014	0.08
Cyclopentane	0.004	0.02
3-Methylpentane	0.008	0.05
n-Hexane	0.012	0.07
Total alkanes (excluding methane)	0.3412	1.28
Ethylene	0.060	0.12
Propene	0.018	0.05
1-Butene + Isobutylene	0.007	0.03
trans-2-Butene	0.0014	0.01
cis-2-Butene	0.0012	Negligible
1-Pentene	0.002	0.01
2-Methyl-1-Butene	0.002	0.01
trans-2-Pentene	0.003	0.02
cis-2-Pentene	0.0013	0.01
2-Methyl-2-Butene	0.004	0.02
Propadiene	0.0001	Negligible
1,3-Butadiene	0.002	0.01
Total alkenes	0.1020	0.29
Acetylene	0.039	0.08
Methylacetylene	0.0014	Negligible
Total acetylene	0.0404	0.08
Benzene	0.032	0.19
Toluene	0.053	0.37
Total aromatics	0.0850	0.56
Total	3.7886	5.43

[a] Determined by multiplying compound concentration by number of carbon atoms in the compound.

TABLE 5-3. AVERAGE AND HIGHEST CONCENTRATION MEASURED FOR VARIOUS AROMATIC HYDROCARBONS IN LOS ANGELES, 26 DAYS, SEPTEMBER THROUGH NOVEMBER, 1966[27]

Aromatic hydrocarbon	Average concentration, ppm	Highest measured concentration, ppm
Benzene	0.015	0.057
Toluene	0.037	0.129
Ethylbenzene	0.006	0.022
p-Xylene	0.006	0.025
m-Xylene	0.016	0.061
o-Xylene	0.008	0.033
i-Propylbenzene	0.003	0.012
n-Propylbenzene	0.002	0.006
3-and 4-Ethyltoluene	0.008	0.027
1,3,5-Trimethylbenzene	0.003	0.011
1,2,4-Trimethylbenzene, and *i*-Butyl-and *sec*-Butylbenzene	0.009	0.030
tert-Butylbenzene	0.002	0.006
Total aromatics	0.106	0.330

(see Section 6) reveal the important influence of mobile source emissions on hydrocarbon mixtures in urban atmospheres.

Among the hydrocarbon oxidation products for which ambient air data were available in 1970, aldehydes were by far the predominating compounds. Total aldehyde concentrations for Los Angeles for 1951 through 1957, as determined by manual, wet-chemical methods, are shown in Table 5-4.[28] Further study in 1960 in the Los Angeles area showed that concentrations of total aldehydes ranged up to 0.36 ppm for a 10-minute sample, with formaldehyde not exceeding 130 $\mu g/m^3$ (0.10 ppm). The maximum acrolein (acrylic aldehyde) value was 25.2 $\mu g/m^3$ (0.011 ppm); but most values were less than half that level. Typical aldehyde concentrations were around 0.10 ppm on many days.[29] Yearly maximum 1-hour average aldehyde concentrations in Los Angeles ranged from 0.20 to 1.30 ppm.

The 1970 report documented the diurnal patterns of nonmethane hydrocarbons for several cities, showing that in most of the urban areas sampled maximum HC concentrations coincided with the peak traffic period of about 6- to 9-a.m. These diurnal patterns, illustrated in Figure 5-1,[22] do not parallel the diurnal variations in secondary contaminants, particularly ozone. Instead, secondary pollutants typically show a pronounced maximum in the afternoon.[2] Insufficient data were available in 1970 to determine seasonal variations in hydrocarbon concentrations nationwide. Data available then for 17 California cities showed, however, that in 14 of those cities maximum HC concentrations (averages of maximum hourly averages) occurred in October or November, presumably as a consequence of the similar meteorological conditions that prevail along the California coast.[2]

TABLE 5-4. RANGE OF YEARLY MAXIMUM 1-HOUR AVERAGE CONCENTRATIONS OF ALDEHYDES, LOS ANGELES COUNTY STATIONS, 1951 THROUGH 1957[28]

Year	Concentration range, ppm	
	Formaldehyde	Total aldehydes
1951	0.05 - 0.12	0.26 - 0.67
1952		0.20 - 0.27
1953		0.25 - 1.20
1954		0.39 - 0.80
1955		0.47 - 1.28
1956		0.51 - 1.30
1957		0.27 - 0.47

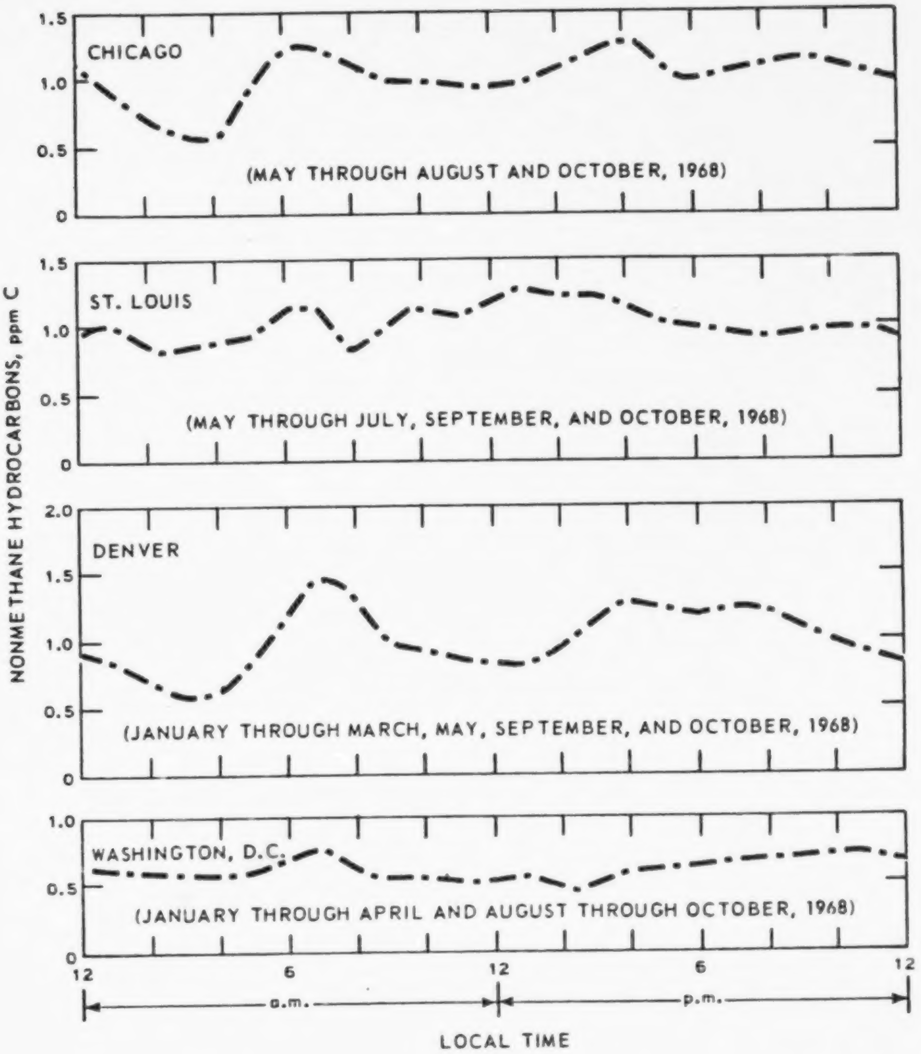


Figure 5-1. Nonmethane hydrocarbons by flame ionization analyzer, averaged by hour of day over several months for four cities.[29]

Diurnal variations in aldehyde concentrations display an early rise, a broad plateau or maximum through most of the day, and a decrease in the afternoon. This pattern is shown for formaldehyde and acrolein concentrations in Los Angeles in Table 5-5,[30] for 1961, and in Figure 5-2,[31] for 1968.

5.5 HYDROCARBON/OXIDANT RELATIONSHIPS

National ambient air quality standards regulate the concentrations of criteria pollutants in the air. They do not directly regulate emissions, though emissions are controlled in order to meet NAAQS. In the case of measurements of ambient air concentrations of hydrocarbons, such measurements do not necessarily reflect emissions of hydrocarbons. At any given time that an urban atmosphere is being measured, the hydrocarbon concentrations measured may represent just one point in time--and space--during a dynamic process that involves the mixing of fresh hydrocarbon emissions (1) with already-reacted (and thus chemically transformed) hydrocarbons, (2) with relatively unreactive or slowly reactive hydrocarbons, and (3) with many other pollutants under various changing meteorologic conditions. Consequently, the major problem facing atmospheric chemists in 1970, including the authors of the air quality criteria document, was that of relating hydrocarbon emissions to resulting oxidant air quality by means of relationships based on ambient air concentrations of hydrocarbons. The criteria document stated:[2]

> The development of a model to relate emission rates of hydrocarbons to ambient air quality and then to the secondary products of photochemical reactions has proved to be an elusive problem. Because of this lack of an appropriate model, the relationship between hydrocarbon emissions and subsequent maximum daily oxidant levels must be approached empirically. The empirical approach adopted is a comparison of 6 to 9 a.m. average hydrocarbon values with hourly maximum oxidant values attained later

TABLE 5-5. AVERAGE FORMALDEHYDE AND ACROLEIN CONCENTRATIONS BY TIME OF DAY IN LOS ANGELES, SEPTEMBER 25 THROUGH NOVEMBER 15, 1961[30]

Sampling time	Formaldehyde		Acrolein	
	Number of days	Average concentration, ppm	Number of days	Average concentration, ppm
7:00 a.m.	7	0.041	2	0.007
8:00 a.m.	18	0.043	3	0.009
9:00 a.m.	21	0.045	3	0.009
10:00 a.m.	28	0.044	5	0.008
11:00 a.m.	27	0.051	5	0.008
Noon	23	0.044	3	0.005
1:00 p.m.	25	0.041	7	0.008
2:00 p.m.	27	0.034	5	0.007
3:00 p.m.	25	0.026	4	0.004
4:00 p.m.	15	0.019	5	0.004

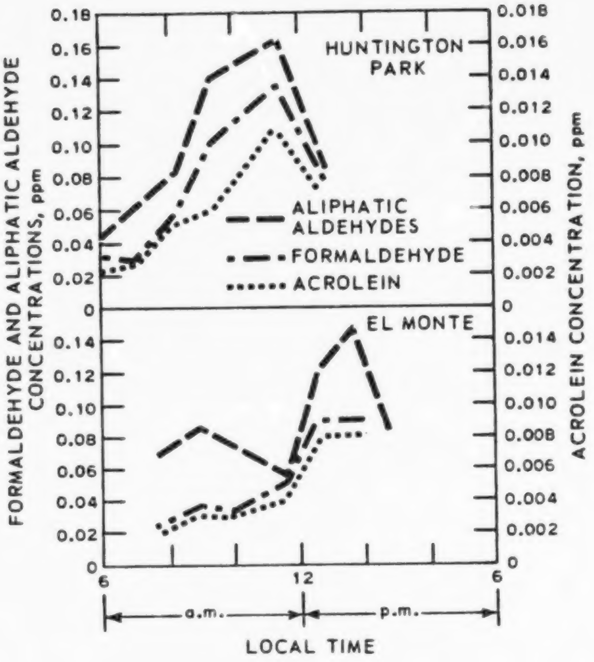


Figure 5-2. Hourly aldehyde concentrations at two Los Angeles sites, October 22, 1968.[31]

> in the day. This approach has validity only because of the dominating influence of the macro-meteorological variables on both the concentrations of precursors and photochemical products. Furthermore, this approach can yield useful information only when a large number of days are considered; this guarantees the inclusion of all possible combinations of emission rates, meteorological dilution and dispersion variables, sunlight intensity, and ratios of precursor emissions. When maximum daily oxidant values from such an unrestricted data base are plotted as a function of the early morning hydrocarbons, a complete range of oxidant values--starting near zero and ranging up to finite and limiting values--is observed. Given data for a sufficient number of days, it becomes apparent that the maximum values of attainable oxidant are a direct function of the early morning hydrocarbon concentration. This upper limit of the maximum daily oxidant concentration is dependent on the metropolitan geographical area only to the extent that differences in meteorological variables exist between these areas. Thus the data from all cities can be plotted on one graph when defining the oxidant upper limit as a function of early morning hydrocarbon.[2]

As the document further noted, all available data relating directly measured nonmethane hydrocarbon concentrations to maximum daily oxidant concentrations were used.[2] For Los Angeles, however, no nonmethane data were available; and for some stations in each of the other cities nonmethane hydrocarbon concentrations were derived by applying an empirically determined ratio between total and nonmethane hydrocarbons.[32,33] Figure 5-3 shows maximum oxidant concentrations as a function of 6-to-9-a.m. average total hydrocarbon concentrations, developed from 326 days of data obtained from five cities. Direct examination of the data used to develop this plot shows that, at any given hydrocarbon level, there appears to be a limit to the amount of oxidant that can be generated.[32] Specifically, the data appear to indicate that an average 6-to-9-a.m. concentration of 0.3 ppm nonmethane hydrocarbon (expressed as carbon) can be expected to produce a maximum hourly average oxidant concentration of up to 0.1 ppm.[32] It must be borne in mind, however, that the aerometric data base underlying this model was obtained by FID measurements that were subject to all the errors associated with this method.

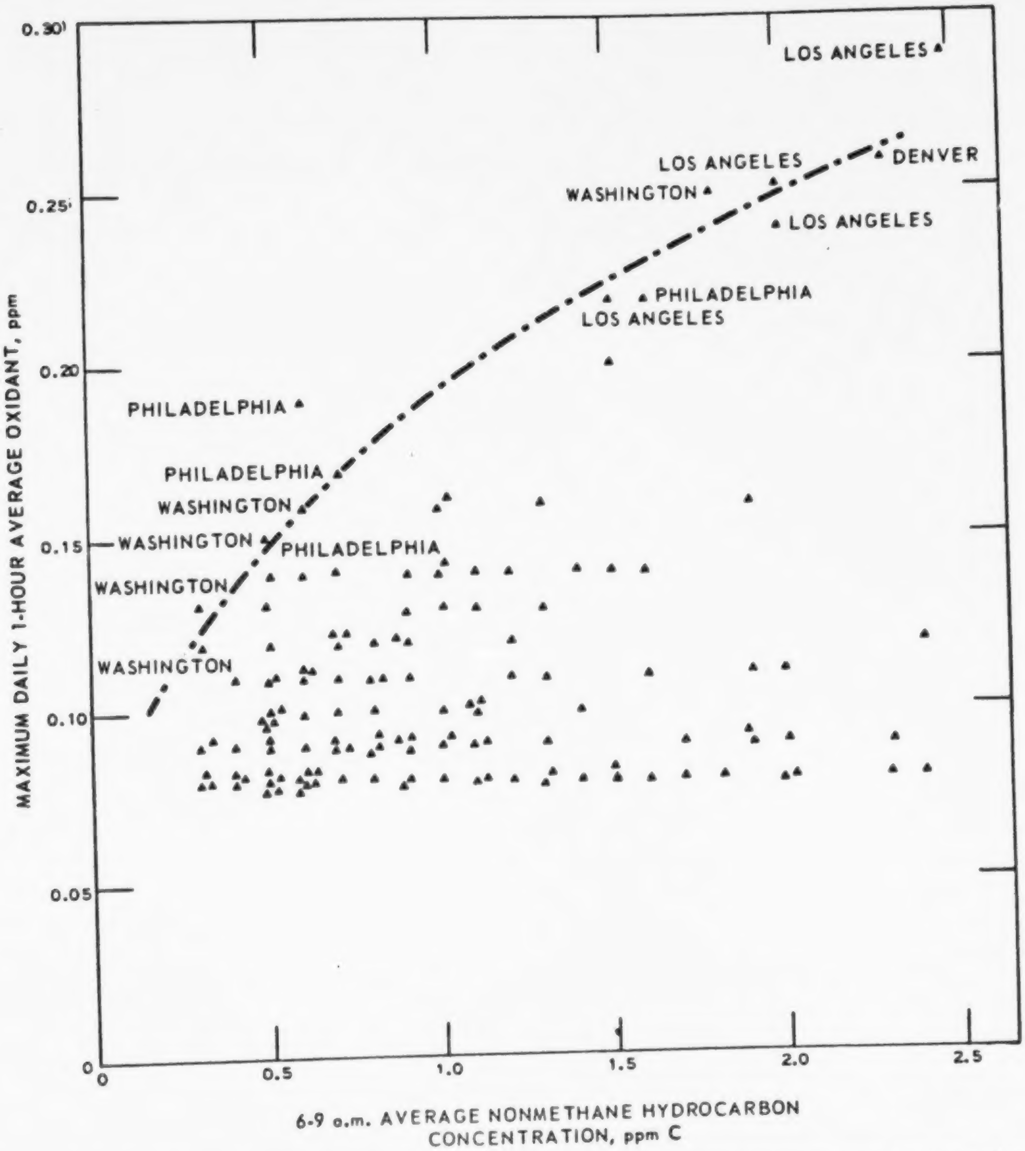


Figure 5-3. Maximum daily oxidant as a function of early morning nonmethane hydrocarbons, 1966-1968 for CAMP stations; May through October 1967 for Los Angeles.[2]

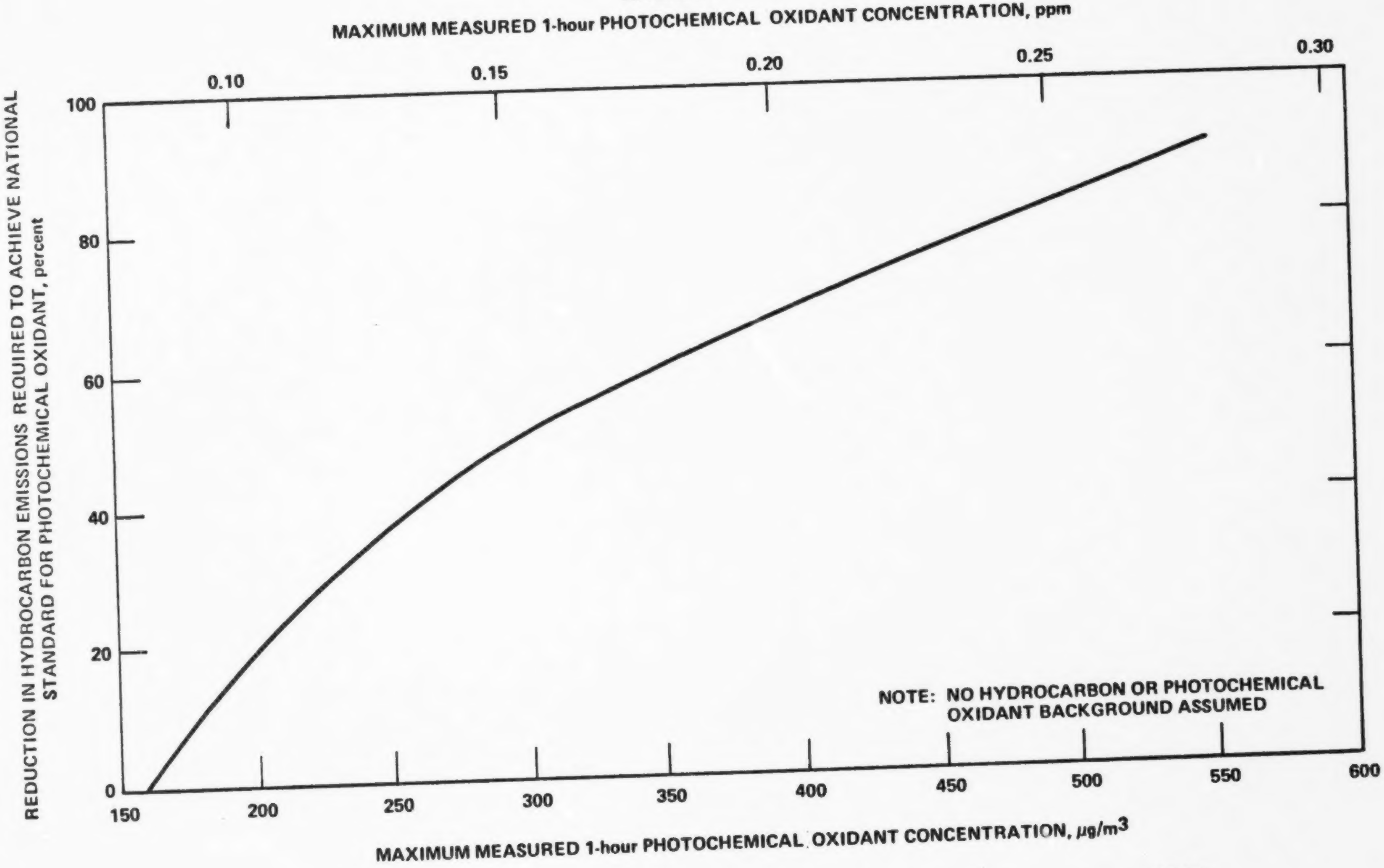
A number of caveats for this method of relating hydrocarbon concentrations to oxidant concentrations were given in the 1970 hydrocarbon document,[2] in the 1971 air quality criteria document for nitrogen oxides,[33] and in the journal publication that described the development of the upper-limit curve of Figure 5-3.[32] Schuck et al.[32] clearly stated that the upper limit curve is descriptive rather than predictive. It defines the limit on oxidant associated with certain levels of ambient hydrocarbons but cannot predict or explain this observed relationship.[32] The nitrogen oxides document of 1971, which discussed the upper-limit curve in detail, noted that the derivation of an upper limit curve requires abundant measurements. "Since the upper limit is attained on only about 1 percent of the days in a year, many days' measurements are needed in order to provide reasonable assurance that an upper-limit point has actually been observed."[33] The relative paucity of data at the actual curve in Figure 5-3 demonstrates this point.

Nevertheless, since the hydrocarbon standard was promulgated for the purpose of ensuring the attainment and maintenance of the oxidant standard, EPA had to prescribe a method for determining the relationship between hydrocarbon emissions and resulting ambient air concentrations of oxidant. In response to that need, EPA scientists developed a method that used the upper-limit curves in conjunction with the dispersion-related equations used in linear rollback models.[7]

Rollback models embody the principle that reductions in emissions of a pollutant are reflected by improvements in air quality, as may be shown by a straight line, a curved line, or a complex surface that expresses some proportionality relationship.[9] Linear rollback, though it would result in improved oxidant air quality, does not accurately describe the relationship between hydrocarbons and oxidant air quality; it is best applied to pollutants that, unlike hydrocarbons, do not undergo chemical transformations in the atmosphere.[9] Consequently, EPA used the upper-limit curve to derive a type of modified rollback model for relating maximum 1-hour photochemical oxidant concentrations to the percentage reduction needed in hydrocarbon emissions in order to achieve the oxidant standard. The resulting model or method was promulgated in 1971 as Appendix J.[34] It represented EPA's best attempt, given the data available and the state of the art of modeling in 1971, to go beyond relating ambient air HC levels to oxidant levels and to attempt the more difficult task of relating hydrocarbon emissions to oxidant levels. The Appendix J curve is shown as Figure 5-4.[33,34] As discussed in Section 6, revision of the NAAQS in 1978 for oxidants and promulgation of an NAAQS for ozone in 1979 led to replacement of the Appendix J model by four other modeling techniques for use by the States in determining hydrocarbon reductions necessary to attain the NAAQS for ozone.

5.6 HEALTH EFFECTS

The document entitled, Air Quality Criteria for Hydrocarbons,[2] which was published in 1970, provided no health effects data directly related to ambient concentrations of gaseous or volatile hydrocarbons as a pollutant class. Excluded from this health assessment were hydrocarbons ($>C_{12}$) and other organics (e.g., polycyclic organic matter) associated only with suspended particles in the atmosphere. The only direct adverse effect at that time attributable to known ambient concentrations of hydrocarbons was the vegetation damage from ethylene; however, these effects were highly dependent on the locality and the species of plants grown for retail sales. The sole purpose of prescribing a nonmethane hydrocarbon air quality standard



NOTE: NO HYDROCARBON OR PHOTOCHEMICAL OXIDANT BACKGROUND ASSUMED

Figure 5-4. Required hydrocarbon emission control as a function of photochemical oxidant concentration.[33,34]

of 160 μg/m^3 (0.24 ppm), maximum 3-hr average concentration (6-to-9-a.m.) not to be exceeded more than once per year, was to control the ambient levels of specific smog components such that the oxidant standard of 160 μg/m^3 (0.08 ppm), maximum 1-hour concentration not to be exceeded more than once a year, would be met.[4] Inherent in the setting of this hydrocarbon standard was the fact that these specific smog components known as "oxidants" are produced from hydrocarbons by gas-phase photochemical reactions involving oxides of nitrogen (NO_x), oxygen, and sunlight. To date, the only health effects reported from exposure to smog products derived directly from hydrocarbons, as opposed to indirectly derived products such as ozone, at levels approximating those found in the ambient air, are the irritating effects of aldehydes and peroxyacylnitrates on mucous membranes of the eyes, nose, and throat. The aldehydes that have been identified as the most effective irritants are acrolein and formaldehyde, while the peroxyacylnitrates identified as such are the acetyl and benzoyl derivatives. These smog components (aldehydes, peroxyacylnitrates) are governed by the control strategy cited in the revisions to the NAAQS for photochemical oxidants.[6]

The lack in 1970 of a health effects data base directly related to hydrocarbons at ambient concentrations, either as individual compounds or as a class, is readily observed from the toxicological and clinical studies discussed below. These studies were those reviewed in the preparation of the 1970 criteria document for hydrocarbons[2] that served as the basis for the promulgation of the standards.

The effects observed up to 1970 for hydrocarbons either as a class or as individual compounds are as follows:

5.6.1 Aliphatic Hydrocarbons

In general, members of this hydrocarbon series are virtually inert and produce no demonstrable pathological effects. The first two members of these alkane hydrocarbons, methane and ethane, are pharmacologically "inert," belonging to a group of gases called "simple asphyxiants." These gases can be tolerated in high concentrations in inspired air; however, above concentrations of 50,000 and 100,000 ppm, one observes systemic effects of ethane and methane, respectively, due to oxygen deprivation or asphyxia. Pharmacologically, the aliphatic hydrocarbons above ethane, both saturated and unsaturated, can be grouped with the general anesthetics in a large class known as the central nervous system depressants. This is particularly true of ethylene, propylene, and acetylene, which have all been used as anesthetics at high concentrations. The vapors of the alkane hydrocarbons are mildly irritating to mucous membranes, the irritation increasing in intensity from pentane to octane. Generally, alkanes from the pentanes (C_5) through the octanes (C_8) show increasingly strong narcotic properties which have been correlated with increased lipophilia. Narcotic effects may be accompanied by exhilaration, vertigo, headache, anorexia, incoordination, and nausea. These compounds in general are relatively inactive toxicologically at concentrations of hundreds to thousands of times above those levels found in the atmosphere. No effects were observed at levels below 500 ppm for the alkanes and 1,000 ppm for the alkenes. These observed effects are summarized in Tables 5-6 and 5-7.[35]

5.6.2 Alicyclic Hydrocarbons

Toxicologically, the alicyclic hydrocarbons, both saturated and unsaturated, are similar to the aliphatic hydrocarbons in that they act as general anesthetics

TABLE 5-6. TOXICITY OF SATURATED ALIPHATIC HYDROCARBONS[35]

Hydrocarbon	Formula	Health effects	Concentration, ppm	% by volume of air	Subject	Ambient concentrations, ppb[a,36]
Methane	CH_4	No systemic effects.	<100,000	10		1300-4000
Ethane	C_2H_6	No systemic effects.	<50,000	5	man	0.05-95
Propane	C_3H_8	No symptoms after brief exposure.	<10,000	1	man	12-94
		Odor not detected.	<20,000	2	man	
		No irritation, but slight dizziness in a few minutes.	<100,000	10	man	
Butane	C_4H_{10}	Odor not detected.	<5,000	0.5	man	0.01-182
		No systemic effects except drowsiness.	10 min. @ 10,000	1.0	man	
Pentane	C_5H_{12}	Threshold limit.	1,000	0.1	man	0.023-64
		Odor readily detectable.	5,000	0.5	man	
		No mucous membrane irritation or other symptoms.	10 min. @ 5,000	0.5	man	
		Narcosis in 5 to 60 min.	90,000-120,000	9-12	mice	
Hexane	C_6H_{14}	Threshold limit.	500	0.05	man	4-27
		No symptoms.	2,000 @ 10 min.	0.2	man	
		Dizziness and sensation of giddiness.	5,000	0.5	man	
		Narcosis.	30,000	3.0	mice	

TABLE 5-6 (continued)

Hydrocarbon	Formula	Health effects	Concentration, ppm	% by volume of air	Subject	Ambient concentrations, ppb[a],36
		Convulsions and death have resulted from exposures of equal duration.	35,000-40,000	3.5-4.0	Mice	
Heptane	C_7H_{16}	Threshold limit.	500	0.05	Man	0.2-34
		Slight vertigo.	1,000 @ 6 min. 2,000 @ 4 min.	0.1 0.2	Man Man	
		Marked vertigo, hilarity, and lack of coordination.	5,000 @ 4 min.	0.5	Man	
		Intoxication characterized by uncontrolled hilarity in some individuals and in others a stupor lasting for 30 min. after exposure. These individuals complained of loss of appetite, slight nausea, and a taste resembling gasoline.	5,000 @ 15 min.	0.5	Man	
		Narcosis.	10,000-15,000 @ 30-60 min.	1-1.5	Mice	
		Convulsions/ death.	15,000-20,000 @ 30-60 min.	1.5-2.0	Mice	
Octane	C_8H_{18}	Threshold limit.	500	0.05	Man	0.04-3.4
		Narcosis in 30-90 min.	6600-13,700	0.66-1.37	Mice	
		No deaths or convulsions.	<13,700 for 30-90 min.	1.37	Mice	

[a] Concentrations appearing in the literature up to 1978.

TABLE 5-7. TOXICITY OF UNSATURATED ALIPHATIC HYDROCARBONS[35]

Hydrocarbon	Formula	Health effects	Concentration, ppm	% by volume of air	Subject	Ambient concentrations, ppb[a,36]
Ethylene	C_2H_2	TLV[b]	1,000	0.1	Man	0.7-700
		MPL[c]	5,500	0.55	Man	
Propylene	C_3H_6	MPL[c]	4,000	0.4	Man	1-52
1-Butene	C_4H_8	MPL[c]	4,000	0.4	Man	1-6
1,3 Butadiene	C_4H_6	TLV[b]	1,000	0.1	Man	1-9
		Only slight eye and upper respiratory tract irritation in man.	8,000 @ 8 hr	0.8	Man	
		No deleterious effects from these exposures; however, the animals were slightly anesthetized, showing a loss of pupillary reflex. Noisy breathing and rales were noted.	200,000-250,000 once a day for 15-21 days	20-25	Rabbits	
2-Methyl-1,3-butadiene (isoprene)	C_5H_8	No narcosis.	20,000 for 2 hr	2	Mice	0.2-2.9
			35,000-40,000	3.5-4.0	Mice	
Acetylene	C_2H_2	MPL[c]	5000	0.5	Man	0.2-227
		Slight intoxicating effect.	100,000	10	Man	
		Marked intoxication.	200,000	20	Man	
		Incoordination.	300,000	30	Man	
		Unconsciousness in 5 min.	350,000	35	Man	

[a] Concentrations appearing in the literature up to 1978.

[b] TLV - Threshold limit value.

[c] MPL - Maximum permissible level.

and central nervous system depressants having a relatively low order of acute toxicity. Cumulative toxicity from repeated exposure to low atmospheric concentrations is unlikely because the alicyclics do not tend to accumulate in body tissues. Massive acute exposure that results in prolonged unconsciousness, anoxia, and convulsions may cause central nervous system sequelae similar to those described as occurring after exposure to volatile aliphatic hydrocarbons. Like the aliphatic compounds, the alicyclic compounds are generally biochemically inert, although not biologically inert and are only reactive at concentrations of 100-1000 higher than those levels found in the ambient air. The vapors in sufficient concentrations will cause irritation of the mucous membranes. In general, the saturated hydrocarbons are less irritating than the corresponding unsaturated compounds. No evidence was found to indicate that alicyclic hydrocarbons are specific hematopoietic toxicants. Like the aliphatic compounds, the alicyclic compounds are generally biochemically inert, though not biologically inert and are only reactive at concentrations of 100 to 1000 higher than those levels found in the ambient air. Data concerning the toxicity of cyclohexane and methylcyclohexane are summarized in Table 5-8.[37]

5.6.3 Aromatic Hydrocarbons

The aromatic hydrocarbons are biochemically and biologically active. The vapors are more irritating to the mucous membranes than equivalent concentrations of the aliphatic or alicyclic hydrocarbons. Systemic injury can result from the inhalation of vapors of the aromatic compounds; no effects, however, have been reported below 25 ppm. This value is 1000 times greater than the average benzene concentration reported in California (Los Angeles) during 1966.

TABLE 5-8. TOXICITY OF ALICYCLIC HYDROCARBONS:
COMPARATIVE EFFECTS OF CHRONIC AND ACUTE EXPOSURE IN AIR[37]

Hydrocarbon	Formula	Health effects	Concentration ppm	Concentration mg/m³	Concentration % by volume of air	Exposure hr	Exposure days	Animal	Type study	Ambient concentrations, ppb[36]
Cyclohexane[a]	C_6H_{12}	No effect.	434	1,491	0.043	8	130	Rabbit	Chronic	3-6
		Minor microscopic changes in kidneys and liver.	786	2,710	0.078	6	50	Rabbit	Chronic	
		No effect.	1243	4,270	0.12	6	50	Monkey	Chronic	
		No fatalities or signs of injury.	3300	11,439	0.33	6	50	Rabbits	Chronic	
		Some fatalities.	7400 18,500	25,419 63,548	0.74-1.85	6	10	Rabbits	Chronic	
		No deaths.	18,500	63,548	1.85	8	1	Rabbits	Acute	
		Deaths.	26,600		2.66	1	-	Rabbits	Acute	
Methylcyclo-hexane[b]	$C_6H_{11}CH_3$	No effect.	241	996	0.024	24	70	Rabbits	Chronic	3-7
		No effect.	1162	4659	0.116	24	70	Rabbits	Chronic	
		No effect.	2800	11,228	0.28	24	70	Rabbits	Chronic	
		Minor evidence of kidney and liver injury.	3300	13,233	0.33	5	70	Rabbits	Chronic	
		No fatalities; lethargy in 50%.	5600	22;456	0.56	6	28	Rabbits	Chronic	
		25% fatalities.	7300	29,273	0.73	6	14	Rabbits	Chronic	
		100% fatalities.	10,000	40,100	1.0	6	14	Rabbits	Chronic	
		100% fatalities.	15,000	60,150	1.5	70 min.		Rabbits	Acute	

[a] The Threshold Limit Value for cyclohexane is 400 ppm.
[b] The Threshold Limit Value for methylcyclohexane is 500 ppm.

It is well established that benzene is an insidious toxicant which has a destructive effect on the hematopoietic system. Experimental evidence indicates, however, that the alkyl derivatives of benzene are not capable of inducing these effects and that benzene is unique among the aromatic hydrocarbons as a myelotoxicant. This difference in toxicity between benzene and its alkyl derivatives has been primarily attributed to detoxification of the derivatives via a different metabolic route. Pharmacologically, the alkyl benzenes or phenylalkanes can be classified with the central nervous system depressants.

Toluene is a more potent narcotic and acute toxicant than benzene, but it does not affect the hematological system.[38] Xylenes are more acutely toxic than benzene or toluene, but, again, they do not affect the hematopoietic system. The comparative effects of acute and chronic exposure to aromatic hydrocarbon vapors in air are shown in Table 5-9.[39]

5.6.4 Hydrocarbon Mixtures

Hydrocarbon mixtures produced and consumed in this country include natural gas, liquid propane gas, petroleum ether, petroleum benzene, petroleum naphtha, gasoline, mineral spirits, kerosene, jet and turbo fuels, and lubricating oils.

Physiological responses resulting from exposure to these hydrocarbon mixtures can be judged from the composition of the mixtures (Table 5-10) and the information given above for physiological responses to the specific hydrocarbons, methane through octane.[40]

Of all the hydrocarbon mixtures, gasoline is undoubtedly the most extensively used and represents a major, nearly homogeneous hydrocarbon mixture that is emitted

TABLE 5-9. TOXICITY OF AROMATIC HYDROCARBONS: COMPARATIVE EFFECTS OF ACUTE AND CHRONIC EXPOSURE IN AIR[39]

Hydrocarbon	Formula	Health effects	Concentration			Exposure		Subject	Ambient concentrations, ppb[36]
			ppm	mg/m³	% by volume of air	hr	days		
Benzene	C_6H_6	TLV	25	80	0.0025	Acute	---	Man	0.025-57
		Mucous membrane irritation.	100	319	0.01	Acute	---	Man	
		Threshold for affecting central nervous system.	370	1,180	0.037	Acute	---	Mice	
		Endurable for 0.5-1.0 hr.	3000	9,570	0.3	Acute	---	Man	
		Prostration.	4700	14,993	0.47	Acute	---	Mice	
		LC 50.	7400	23,606	0.74	Acute	---	Mice	
		Dangerous after 0.5-1.0 hr.	7500	23,925	0.75	Acute	---	Man	
		LC 100.	14,100	44,979	1.41	Acute	---	Mice	
		LC 100.	17,800	56,782	1.78	Acute	---	Rats	
		Fatal after 5-10 min.	20,000	63,800	2.0	Acute	---	Man	

TABLE 5-9 (continued)

Hydrocarbon	Formula	Health effects	Concentration ppm	Concentration mg/m³	Concentration % by volume of air	Exposure hr	Exposure days	Subject	Ambient concentrations, ppb[36]
Toluene	$C_6H_5 \cdot CH_3$	No effect	50-100	188-377	0.05-0.01	Acute	---	Man	0.005-129
		Mild fatigue, weakness, confusion, skin paresthesias.	200	753	0.02	8	1	Man	
		Symptoms more pronounced.	300	1,130	0.03	8	1	Man	
		Symptoms plus mental confusion.	400	1,506	0.04	8	1	Man	
		Also plus nausea, headache, dizziness.	600	2,259	0.06	3	1	Man	
		Also plus loss of coordination, staggering gait, and pupils dilated.	600	2,259	0.06	8	1	Man	
		Same symptoms as above with after-effects characterized by severe nervousness, muscular fatigue, and insomnia.	800	3,012	0.08	8	1	Man	

TABLE 5-9 (continued)

Hydrocarbon	Formula	Health effects	Concentration			Exposure		Subject	Ambient concentrations, ppb[36]
			ppm	mg/m³	% by volume of air	hr	days		
Styrene	$C_6H_5.CH{=}CH_2$	Threshold limit value (TLV).	100	418	0.001	Acute	---	Man	1.5-5
		No effect.	650	2714	0.065	8	180	Guinea pig	
		Eye and nasal irritation only.	1300	5428	0.13	8	180	Rat	
		Eye and nasal irritation only.	1300	5428	0.13	8	180	Rabbit	
		10% deaths.	1300	5428	0.13	8	180	Guinea pigs	
		Some fatalities; varying degrees of weakness, stupor, incoordination, tremor, unconsciousness (in 10 hr).	2500	10,438	0.25	8	1	Guinea pig and rat	
		Unconsciousness in 1 hr.	5000	20,875	0.5	1	1	Guinea pig and rat	
		Unconsciousness in 10 min.; deaths in 30-60 min.	10,000	41,750	1.0	1/2-1	1	Guinea pig and rat	

TABLE 5-9 (continued)

Hydrocarbon	Formula	Health effects	Concentration			Exposure		Subject	Ambient concentrations, ppb[36]
			ppm	mg/m³	% by volume of air	hr	days		
Xylenes (O,M,P)	$C_6H_4.(CH_3)_2$	Threshold for affecting central nervous system.	174	755	0.017	Acute	---	Mice	2.5-119
		Threshold limit value (TLV).	200	868	0.02	Acute	---	Man	
		No hematological effects.	690	2,995	0.069	8	130	Rat and rabbit	
		Decreased leukocytes and red blood cells; increased platelets.	1150	4,991	0.115	8	55	Rabbit	
		Prostration.	4699	20,394	0.469	Acute	---	Mice	
		LC_{50}.	9200	39,928	0.920	Acute	---	Mice	
		LC_{100}.	12,650	54,901	1.26	Acute	---	Mice	
		LC_{100}.	17,250	74,865	1.72	Acute	---	Rat	

TABLE 5-10. PRINCIPAL MIXTURES CONTAINING PARAFFIN HYDROCARBONS[40]

Mixture	Boiling range, °C	Principal paraffins
Natural gas	Gas at room temp.	C_1, C_2
LPG ("bottled gas")	Gas at room temp.	C_3, C_4
Petroleum ether	20-60	C_4 to C_6
Petroleum bezin	40-90	C_5 to C_7
Petroleum naphtha	65-120	C_6 to C_8
Gasoline	36-210	C_5 to C_{10}
Mineral spirits	150-210	C_7 to C_9
Kerosene (coal oil)	170-300	C_9 to C_{16}
Jet and turbo fuels	40-300	C_5 to C_{16}
Lubricating oils	300-700	C_{17} and up

nationwide, whether due to evaporative loss or combustion. Gasoline is a mixture of C_4 to C_{12} hydrocarbons, including paraffins, olefins, naphthenes, and aromatics over a boiling range of 26°C to 204°C (80°F to 400°F). Alkanes and aromatics generally constitute the largest fraction, but olefins and naphthenes are also present. In addition to the 200 hydrocarbons generally contained in gasoline, nonhydrocarbons (additives) are added to improve engine performance. Variations in its hydrocarbon composition do not significantly alter the basic pharmacology and toxicology of gasoline.[41] An acute exposure to gasoline vapors will elicit the symptoms and signs of intoxication described for exposure to heptane. The atmospheric concentrations and the duration of exposure required to elicit these responses will differ, however, with the composition of the gasoline. The concentration of gasoline hydrocarbons that causes mucous membrane irritation will vary with the degree of branching of the paraffins and the content of alkyl derivatives of benzene and olefins. The foregoing does not apply to gasolines that contain a significant concentration of benzene, which appears to be unique among hydrocarbons in its effect on blood-forming tissues. In light of the variability of the composition of gasolines (blends), a single threshold limit value is not applicable; however, as a general rule the contents of the aromatic hydrocarbons and, to a lesser degree, of the additives are used to arrive at the appropriate TLV values.[42] Based on Machle's summary (Table 5-11)[43] of man's response to air concentrations of the volatile fraction (<230°F) of unleaded straight-run gasoline, Gerarde recommended 500 ppm as a TLV for gasoline in 1962.[40]

5.7 WELFARE EFFECTS

Hydrocarbons were recognized as phytotoxic air pollutants at least as early as 1871 as a result of injury to green house plants from illuminating

TABLE 5-11. HUMAN RESPONSE TO GASOLINE VAPORS DISTILLING BELOW 230°F[43]

Concentration, ppm	Exposure time	Response
550	1 hr	No effects.
900	1 hr	Slight dizziness and irritation of eyes, nose, and throat.
2,000	1 hr	Dizziness, mucous membrane irritation, and anesthesia.
10,000	10 min	Nose and throat irritation in 2 min; dizziness in 4 min; signs of intoxication in 4 to 10 min.

gas. Renewed interest in hydrocarbons, and ethylene in particular, occurred in the mid-1950s when ethylene was found to be one of the primary pollutants in the photochemical reaction complex. Although additional combustion sources contribute to ethylene in the atmosphere, the internal combustion engine is the major source of ethylene pollution in metropolitan areas.

The levels of ethylene found in the ambient air vary according to location, time of day, and weather. Low levels in the range of 3 to 5 ppb have been reported for desert areas and Davis, California.[2,44] In contrast, San Francisco air has been reported to contain peaks of 100 ppb for an hour or more on several occasions;[2,45-47] however, the average for that city was 50 ppb in the mid-1960s.[2,45,48] The Pasadena area[49] has, in the past, reported an unusually high value of 500 ppb, while surrounding areas, such as the San Gabriel Valley, have had lower peak values, i.e., 30 ppb.[2,47] Similarily, on the east coast, Washington, D.C., reported average values of 10 to 20 ppb ethylene with maximum values near 60 ppb.[50] In Frederick, Maryland (50 miles west of Washington, D.C.), a rural area at the time, ethylene levels ranged from 1 to 5 ppb.[51]

Research on several unsaturated and saturated hydrocarbons has shown that only ethylene has adverse effects on vegetation at atmospheric concentrations of 1 ppm or less. Concentrations as low as 0.05 ppm have caused malformations in certain plants and injuries to flowers. This concentration is well within the range measured in ambient atmosphere. Other unsaturated hydrocarbons produce similar effects, but at much higher concentrations (Table 5-12).[52] Such concentrations are orders of magnitude higher than the concentrations of ethylene found in the atmosphere.

Research has demonstrated that ethylene is produced naturally within tissues of plants and serves as a hormone in regulating growth and development and other processes such as the ripening of fruit. Thus, ethylene is unique

TABLE 5-12. COMPARATIVE PHYTOTOXICITY OF UNSATURATED CARBON GASES[52]

	Minimum concentration of gas producing response, ppm	
Gas	Sweet pea[a]	Tomato[b]
Ethylene	0.2	0.1
Acetylene	250	50
Propylene	1,000	50
Carbon monoxide	5,000	500
Butylene		50,000

[a] Effect noted: declination in sweet pea seedlings (3-day exposures).

[b] Effect noted: epinasty in tomato petiole (2-day exposures).

in being an endogenous plant-growth regulator and a serious phytotoxic air pollutant. A delicate balance between auxin and ethylene in the petiole is required for normal defoliation; however, an artificial increase in ethylene through pollution would upset this balance and cause early abscission or defoliation without noticeable leaf injury. Unfortunately, this plant-growth inhibitory effect does not characterize ethylene, because other pollutants at sublethal dosages, as well as some diseases and environmental factors, may also inhibit growth. The various effects corresponding to different levels of ethylene are illustrated in Table 5-13.[2]

It should be emphasized that data on the phytotoxicity of ethylene were not used in promulgating a secondary or welfare standard for hydrocarbons, but, like the primary standard, the secondary standard was based on the specifications of the oxidant standards, which automatically fixed the hydrocarbon standards. Prior to 1970, various standards for acceptable levels of ethylene were proposed or adopted. In 1962, the State of California adopted ambient air quality standards for ethylene of 500 ppb (575 $\mu g/m^3$) for 1 hour or 100 ppb (115 $\mu g/m^3$) for 8 hours. These are considered "adverse" levels, based on the damage to vegetation.[53-55] The American Industrial Hygiene Association (ACGIH) has also proposed air quality standards for ethylene.[56] Based on insufficient data at that time, these latter standards were never unequivocally adopted and served only as guidelines. The recommended standards are given in Table 5-14.[56]

TABLE 5-13. DOSAGE-RESPONSE RELATIONSHIPS OF VARIOUS PLANTS TO ETHYLENE[2]

Response	Dosage		Time
	μg/m^3	ppm	
Abscission			
Cotton leaves, square	46-3,435	0.04-3.0	Not stated
Cotton leaves	685	0.6	1 month
Pepper and tomato flower buds	115	0.1	Less than 8 hr
Rose leaves	345	0.3	120 hr
	11,450	10.0	24 hr
Snapdragon petals	575	0.5	1 hr
Chlorosis on leaves			
Cotton (slight)	685	0.6	1 month
Cowpea	2,290	2.0	1 day
Rose	1,145	1.0	5 days
Death of plant			
Cowpea	2,290	2.0	10 days
Dry sepal injury			
Orchids (severe)	115	0.1	8 hr
Orchids (typical)	46	0.04	8 hr
	23	0.02	24 hr
Orchids (slight)	5.75	0.005	24 hr
	345	0.3	1 hr
	57.5	0.05	6 hr
	11.5	0.01	24 hr
Epinasty			
African marigold	1.15	0.001	20 hr
Various plants	345	0.3	24 hr
	3,435	3.0	3 hr
	2,290	2.0	10 days
Flowers do not open			
Carnation	115	0.1	3 days
Orchid	575-1,145	0.5-1.0	20 hr
Flowers close			
Carnation	115	0.1	6 hr
	575	0.5	12 hr
Growth inhibition			
Cotton	685	0.6	1 mo
	46-3,435	0.4-3.0	Not stated
Lily family	860	0.75	7 days
Various plants	2,390	2.0	10 days
Loss of apical dominance			
Cotton	46-3,435	0.04-3.0	Not stated

TABLE 5-14. AMERICAN INDUSTRIAL HYGIENE ASSOCIATION RECOMMENDED STANDARDS FOR ETHYLENE[56]

	1-hr max[a]		8-hr max[a]	
	μg/m³	ppm	μg/m³	ppm
Rural	287.5	0.25	57.5	0.05
Residential	575	0.50	115	0.10
Commercial	862.5	0.75	172.5	0.15
Industrial	1,150	1.00	230	0.20

[a] The rural concentrations should not produce adverse effects in the most sensitive plants. The residential concentrations should produce only slight injury to the most sensitive plants.

6. SCIENTIFIC DATA BASE ON HYDROCARBONS, 1970 THROUGH PRESENT

6.1 CONTRIBUTION OF HYDROCARBONS TO OXIDANT FORMATION

A brief and highly simplified summary of the role of hydrocarbons in the formation of photochemical oxidants was presented in Section 5.1. Since publication of the 1970 criteria document on hydrocarbons, research has produced new findings in the area of reaction mechanisms but has consistently substantiated the basic chemistry of oxidant formation as presented in the 1970 document. The new findings and their significance have been discussed in detail in three recent reviews, Ozone and Other Photochemical Oxidants, Air Quality Criteria for Ozone and Other Photochemical Oxidants, and Air Quality Criteria for Nitrogen Oxides.[8] Consequently, only brief mention is made here of the significant research findings of the past decade.

A major accomplishment in recent years is the development of computer techniques for simulating the atmospheric smog-forming process.[57,58] Such techniques have provided a useful tool for identifying and studying those reactions that play a key mechanistic role and for predicting potentially important but as yet unidentified reaction products in the ambient atmosphere.[7]

The most important mechanistic finding of recent years is that the hydroxyl radical ($OH^{\cdot}$) is responsible for much of the oxidation of hydrocarbons and aldehydes in the atmosphere.[59,60] Hydroperoxy ($HO_2^{\cdot}$) and alkylperoxy ($RO_2^{\cdot}$) radicals have also been identified as having major roles in the oxidation of NO to NO_2, and some sources of these radicals in the atmosphere have been identified.[7] In addition, more complete information is now available to account for the degradation of organic oxidant, the oxidation of NO to NO_2, and the formation of organic products in the ambient atmosphere, for paraffinic and olefinic reactants though not for aromatics.[7] Another noteworthy mechanistic finding is that some nitrogenated components of the photochemical smog system, e.g., peroxyacetyl nitrate (PAN), may have greater roles in atmospheric photochemical processes than thought earlier.[7]

In addition to new information on reaction mechanisms involving hydrocarbons, new reaction products of photochemical processes have been identified or postulated, including organic compounds and a number of inorganic nitrogenous acids.[7]

Three additional areas of hydrocarbon air chemistry have been the subjects of rather extensive research over the past decade: (1) the role of gas-phase natural hydrocarbons in photochemical processes; (2) the role of gas-phase hydrocarbons in the formation of secondary organic aerosols; and (3) the contribution of gas-phase hydrocarbons to the oxidation of sulfur dioxide and the consequent production of acidic precipitation.

The role of natural hydrocarbon emissions in photochemical processes and reactions, which is a topic of major importance in the context of ozone control strategies, was treated in detail in _Air Quality Criteria for Ozone and Other Photochemical Oxidants_[7] and will again be addressed when that document is revised. The question of the role of gas-phase hydrocarbons in the formation of secondary organic aerosols is treated at length in the NAS document, _Ozone and Other Photochemical Oxidants_,[9] and in some detail in _Air Quality Criteria for Sulfur Oxides and Particulate Matter_;[61] but will be briefly summarized here to demonstrate the diversity and divergent chemical behavior of individual species within the class of compounds known as hydrocarbons. Likewise, the formation and effects of acidic precipitation are discussed in _Air Quality_

Criteria for Nitrogen Oxides,[8] but the role of hydrocarbons in contributing free radicals that oxidize sulfur dioxide (SO_2) to sulfur trioxide (SO_3), from which sulfuric acid is formed in the atmosphere, is not discussed in that document and thus will also be summarized here.

Secondary organic aerosols are aerosols containing organic compounds that are formed in the atmosphere by means of gas-phase photochemical reactions involving the primary pollutants, hydrocarbons and nitrogen oxides, and a secondary pollutant, ozone. Using a chemical-element balance technique that he developed, Friedlander[62] estimated that secondary organic aerosols accounted for 76 percent and 82 percent of the aerosol carbon in 2-hour and 24-hour samples, respectively, in Pasadena, California, in September 1973. During a severe photochemical episode in which the ozone maximum was 0.67 ppm, secondary organics reached as high as 95 percent of the total ambient air organics.[62]

Investigations into the chemical composition of secondary organic aerosols, which necessitate the use of sophisticated techniques and instrumentation, have shown that carboxylic acids and dicarboxylic acids abound, along with lesser amounts of other aliphatic di- or multifunctional oxygenated compounds, aromatic monofunctional oxygenated compounds, and terpene-derived oxygenates.[61-67] Most of the compounds are difunctional compounds that could arise through the photochemical oxidation of cyclic alkenes and alkadienes.[9] Ambient air data on gas-phase organics and on aerosols reveal that organics always account for an important fraction of urban aerosols, but that only a small fraction of the gas-phase organics in ambient air is converted into particulate matter.[9,68]

In view of these two facts, researchers have sought to identify those specific hydrocarbons and other organics that generate aerosols. Smog chamber studies have been conducted using mixtures of hydrocarbons irradiated in the presence of nitric oxide or nitrogen dioxide or both in "clean" air, in ambient air, and with and without the addition of sulfur dioxide, water, and ammonia. These smog chamber studies have shown that, in the absence of sulfur dioxide (the presence of which would result in inorganic aerosols), aerosol formation depends strongly on the type of precursor hydrocarbons irradiated. The trends observed from smog chamber data and from examination of vapor-pressure/volatility data are enumerated below.[9]

1. A threshold concentration exists for each hydrocarbon precursor, below which no organic aerosol is formed.
2. Most paraffinic hydrocarbons, even at high concentrations, do not generate aerosols when irradiated. However, the more reactive, higher branched-chain paraffins (>6 carbon atoms) will generate aerosols if irradiated for a long time.
3. Acetylenics do not form aerosols.
4. Carbonyl compounds (ketones, C_1-C_7 aldehydes, dialdehydes) do not generate aerosols.
5. The role of aromatic hydrocarbons in generating aerosols remains uncertain because conflicting data have been reported. Threshold concentrations for any aromatics that may form aerosols remain unknown as well.
6. At high concentrations, all unsaturated hydrocarbons can form organic aerosols when reacted with ozone.
7. At parts-per-million concentrations, alkenes having fewer than six carbon atoms do not form aerosols. Aerosol data obtained with higher concentrations of these low-molecular-weight alkenes cannot be extrapolated to atmospheric concentrations.
8. At lower concentrations (1 to 10 ppm), the chain length of alkenes produces a marked effect on aerosol formation. Alkenes with more than six carbon

atoms form aerosols provided scission of the double bond(s) yields a fragment of five or more carbon atoms.

9. Threshold concentrations for >C_7 alkenes are in the parts-per-million to parts-per-hundred-million range; and determination of their gas-phase concentrations is necessary for any assessment of their contributions to secondary organic aerosols.

10. Cyclic olefins and diolefins form aerosol even when present at low concentrations. Cyclic olefins and diolefins from much more aerosol per unit of precursor than 1-alkenes that have the same carbon number. The same effect of chain length and double-bond position is observed for cyclic diolefins as for alkenes.

These data on aerosol precursors are summarized in tabular form in Section 6.5.1 (Table 6-27). Ambient air concentrations of those compounds that can generate aerosols are given in Section 6.4, along with the ambient air concentrations of other gas-phase hydrocarbons.

Hydrocarbons have not only been implicated in the production of secondary organic aerosol but also in the production of urban sulfate aerosol and ultimately in the acidification of rain. The acidification of rain and snow is directly caused by acids, namely, hydrochloric, sulfuric, and nitric. Hydrochloric acid may be directly emitted from coal fired power plants; however, the latter two acids are initially emitted as the respective anhydrides (SO_2 and NO_2) and are transformed to sulfuric and nitric acids during atmospheric transport by a complex series of chemical reactions.

Oxidation of SO_2 in the atmosphere can either take place in the gas phase[69] or in solution.[70] Both processes contribute to the presence of sulfate in cloud water and rain water. The acidification of rain is principally due to oxidation of SO_2 in cloud droplets and rain drops, the absorption of free gaseous acids (e.g., SO_2) by droplets and raindrops, or the scavenging of acid aerosol by the falling raindrops. A series of potential gas-phase reactions by which SO_2 may possibly be oxidized in the atmosphere is depicted in Table 6-1.[71] Results of recent chemical rate studies of SO_2 oxidation in water[72] were extrapolated to sulfate formation in water droplets under atmospheric conditions using oxygen, ozone, and hydrogen peroxide (H_2O_2) as the oxidants. Extrapolation of these laboratory data indicates that in a relatively clean atmosphere (5 ppb SO_2, 50 ppb O_3, 1 ppb H_2O_2) the favored oxidizing agent is H_2O_2 rather than O_3 or O_2, provided the pH is less than 5.5. Overall, both of these reactions probably contribute to worldwide urban sulfate production on a large scale, and ultimately, to the acidification of rain.

This information bears on the broader problem of the potential welfare effects of acidic precipitation, which are discussed briefly in Section 6.7.

It is apparent from the examples cited above that information generated since the 1970 criteria document was issued has provided a much more complete view of probable atmospheric oxidant formation processes and the role of organic compounds in those and other atmospheric processes, though much of the evidence for reaction mechanisms has been obtained from laboratory studies and remains to be verified in the ambient atmosphere. The elucidation of atmospheric reaction mechanisms, along with other research of the past decade, has confirmed that photochemical oxidants in the ambient air are a function of the presence of hydrocarbons, as well as other organic compounds and nitrogen oxides, in the atmosphere.[7-9]

6.2 MEASUREMENT METHODOLOGY

The essential features of the 1971 Federal Reference Method for the measurement of nonmethane hydrocarbons were described in Section 5.2.

TABLE 6-1. POSSIBLE ATMOSPHERIC GAS PHASE SO_2 OXIDATION PROCESSES[71]

Initial Steps

(1) $SO_2 + h\nu(2400\text{-}3400\text{Å}) \rightarrow SO_2$

(2) $SO_2 + O_2 \rightarrow (SO_4)$

(3) $SO_2 + O + M \rightarrow SO_3 + M$

(4) $SO_2 + O_3 \rightarrow SO_3 + O_2$

(5) $SO_2 + NO_3 \rightarrow SO_3 + NO_2$

(6) $SO_2 + N_2O_5 \rightarrow SO_3 + N_2O_4$

(7) $SO_2 + CH_3O_2 \rightarrow SO_3 + CH_3O$

(8) $SO_2 + HO_2 \rightarrow SO_3 + OH$

(9) $SO_2 + OH + M \rightarrow HSO_3 + M$

Possible Subsequent Reactions

(10) $SO_3 + H_2O \rightarrow SO_3 \cdot H_2O \rightarrow H_2SO_4$

(11) $SO_3^{\cdot} + H_2O \rightarrow$ nucleus

(12) $HSO_3^{\cdot} + OH \rightarrow H_2SO_4$

(13) $HSO_3^{\cdot} + OH \rightarrow H_2O + SO_3$

(14) $HSO_3^{\cdot} + HSO_3^{\cdot} \rightarrow H_2S_2O_6$

(15) $HSO_3^{\cdot} + H_2O \rightarrow HSO_3^{\cdot}\,(H_2O)$

(16) $HSO_3^{\cdot} + O_2 \rightarrow HSO_5$

(17) $HSO_4^{\cdot} + H_2O \rightleftarrows HSO_5^{\cdot}\,(H_2O)$

Instrumentation for total and nonmethane hydrocarbon measurements by flame-ionization detection has not changed appreciably since 1971. For that reason, this section mainly presents a critique of the method, based largely on work done since 1971; and presents some of the problems associated with the application of mass measurements of hydrocarbons. In addition, information is presented on the use of gas chromatographic techniques for hydrocarbon measurement and on developments since 1971 in FID measurement methods.

The EPA reference method for nonmethane hydrocarbons (NMHC) involves the gas chromatographic separation of methane from total hydrocarbons in an air sample. This is followed by FID measurement of the separated methane and of total hydrocarbons containing methane, in aliquots of the same air sample.[5] The concentration of NMHC is obtained by subtraction of the methane measurement value. Presently available commercial analyzers are still based on these principles and provide a measurement of total "nonmethane hydrocarbons" by subtraction of separate measurements of total hydrocarbons (THC) and methane in an FID. Methane is measured apart from THC in one of two ways, either by separation in a chromatographic column or by selective oxidation in a heated oxidizer.[12,14] The chromatographic separation of methane that is used in the originally promulgated Reference Method represents a significant improvement in methodology over the separation technique used prior to 1970. The catalytic, selective oxidation of nonmethane hydrocarbons to carbon monoxide in a heated oxidizer makes it possible to determine methane separately. By subtracting the FID value for methane from the measurement of THC, the NMHC concentration is obtained.[12,14] In recognition of the fact that the FID responds to organically bound carbon in compounds other than hydrocarbons, the measurement of NMHC is now referred to as nonmethane organic compound (NMOC) measurement. This nomenclature is more accurate than the previous nomenclature and will be used where appropriate in the remainder of this section.

Studies of the FID Federal Reference Method, using commercial analyzers, have been reviewed in a recent EPA draft report and two such studies are cited here from that report.[73]

The first of the two studies involved the analysis of known synthetic mixtures of NMHC in compressed air cylinders by 16 different users of the reference method.[74] The NMHC concentrations tested were 0.23 and 2.90 ppm C. As shown in Table 6-2, the majority of the measurements of the lower concentration, which was near the HC NAAQS level of 0.24 ppm C, were in error by 50 to over 100 percent. At 2.90 ppm C, the majority of the measurements were in error by only 0 to 20 percent. Thus, the higher the concentrations measured, the better the accuracy. The major causes of error were the inability of the instrument to measure low levels of NMHC; the complexity of the instrumentation; and the inability of the average user to identify and correct problems.

Table 6-2 PERCENTAGE DIFFERENCE FROM KNOWN CONCENTRATIONS OF NONMETHANE HYDROCARBONS OBTAINED BY SIXTEEN USERS[74]

Known NMHC concentration	Percent				
	>100	50-100	20-50	10-20	0-10
0.23 ppm	6	4	3	2	1
2.90 ppm	2	--	3	2	9

In the second study, aliquots of the same ambient air sample were measured with five different commercial FID instruments operated by skilled personnel.[75] Results from different analyzer pairs agreed within 0.1 to 0.5 ppm C. Although these differences represent only 1 to 5 percent of the full scale of the instrument (0 to 10 ppm, the range necessary to include all ambient air HC values), and are normal errors for ambient air monitoring, they are quite large relative to the NAAQS of 0.24 ppm C. As these two studies show, even under optimum operating conditions, agreement between instruments and measurements is poor at low concentrations.[73]

In a fairly recent study conducted for EPA, the reference method was subjected to a comprehensive evaluation that included testing of six commercial FID instruments. Generally, results showed poor performance; the major problems were wide differences in response to different NMHC species and discrepancies that were apparently related to variations in ambient relative humidity.[76]

In its assessment of the flame ionization detection method and instruments based on that method, EPA summarized the problems as follows:[14]

1. The FID responds non-uniformly to various organic compounds.
2. The FID response varies with design and operating conditions.
3. The normal FID response is roughly proportional to the "carbon number" of the compound, but otherwise has little or no relationship to the photochemical reactivity of the compound.
4. Normal instrumental variability errors are substantially increased by the need to subtract two separate and independent measurements and by the need for higher scale ranges to accommodate the THC and methane concentrations, which can be much higher than the NMOC difference.
5. The FID is susceptible to zero drift and possible interference from water vapor.

6. Calibration procedures have not been standardized and calibration may be based on methane, propane, or other compounds depending on analyzer design or operator preference.
7. The FID requires hydrogen, which presents a degree of operational hazard.
8. Analyzers using chromatographic separation of methane are operationally complex and require higher levels of operator training and effort to maintain than most other types of ambient monitors. These problems appear to limit the useful sensitivity of currently available analyzers to a few tenths of 1 ppm (methane equivalent).

The major limitations of the FID measurement method for hydrocarbons result in some very practical and pertinent consequences that must be mentioned, if only briefly. First, the high measurement error associated with the method results in erroneous values for hydrocarbon concentrations in ambient air. This is particularly true for concentrations in the range of the present NAAQS for hydrocarbons. This measurement error must be kept in mind when NMHC ambient air data are compared with exposure data from human or animal toxicity studies. In addition, the errors associated with FID measurements limit the confidence that can be placed in the use of the FID method for routine monitoring and in the use of FID data for predictive purposes or for verification of air quality trends of emission inventory accuracy. It should be noted, however, that at higher NMOC levels, e.g., those required for predictive models such as EKMA (Section 6.5), the errors in NMOC measurements made by current methods are commensurate with the variability of the models, because the models themselves have limited precision arising from necessary assumptions, estimates, and simplifications.[14] In many cases, the same NMOC methods have been or will be used to develop or establish the model.[14]

Second, the FID technique produces measurements of total mass of NMOC in ambient air. Measurement of the mass of total NMOC in ambient air, however, is of somewhat limited utility in the overall control of ozone air quality. This limited utility is related to four factors: (1) Other volatile organic compounds besides hydrocarbons are photochemically reactive but, even if detected, their mass is not quantitatively measured by the FID method. (2) The measurement of hydrocarbon mass alone does not give any indication of the reactivity with respect to ozone formation of the hydrocarbon mixture measured. (3) Mass measurements cannot be related to the molar concentration of total hydrocarbons in the air sampled. (4) Total hydrocarbon mass, without identification of individual hydrocarbons, does not permit identification of those sources that contribute most heavily to ozone formation. As stated in the 1970 criteria document for hydrocarbons:

> As a consequence of the different reactivities of individual hydrocarbons, it is impossible to predict accurately the rate of consumption of hydrocarbons in photochemical air pollution unless the detailed composition of the hydrocarbon component is known or can be estimated. Knowledge of the total concentration of hydrocarbons is insufficient, since two atmospheres having the same total hydrocarbon measurement may contain individual hydrocarbons of very different reactivity and thus exhibit very different rates of hydrocarbon consumption and photochemical air pollution development.[5]

An EPA study on reactivity of hydrocarbons from mobile sources concluded that since "hydrocarbons do not participate to the same extent in atmospheric reactions leading to oxidant formation, methods for measurement of more than mass of emissions are necessary to project adequately the impact of mobile sources on photochemical pollution."[77] The same is true with respect to the impact of HC emissions from other sources. It is apparent that FID measurements are inadequate for the complete characterization of hydrocarbons in ambient air.

There are applications, however, for which mass measurements of NMOC must be obtained and for which total NMOC concentrations are the best available measure of the oxidant-forming potential of organic compounds in the ambient air. Studies are under way in EPA to develop better methodology for NMOC measurements for such applications.[78]

Consequently, modifications of the FID method as well as the development of other NMOC methods are in progress, though these methods and techniques will probably not be available for routine use for several years. These developments are briefly summarized below.[12,14,78]

In a variation of the present method for chromatographic separation of methane from nonmethane hydrocarbons, chromatographically separated nonmethane organics are backflushed and are converted to CO_2 rather than methane. The CO_2 is then measured by conventional infrared methods. This technique is presently used to measure source concentration levels. It is a direct measurement of NMOC, avoids the FID response problems, and does not require hydrogen. It has, however, the operational problems of a chromatograph as well as the sensitivity and response-time problems associated with low-level infrared CO_2 measurement.[14,78]

Another method for measuring methane is gas filter correlation, an optical technique which can detect methane specifically without prior separation from other ambient gases. The total hydrocarbon concentration is measured conventionally by FID, and the NMOC concentration is obtained by difference. This technique may prove to be a useful alternative to the currently available selective oxidation technique, but otherwise promises no substantial advantages.[14]

In another approach, which is currently under consideration by EPA, an ambient air sample is passed through a scrubber which has been shown to eliminate

>99.98% (330 ppm is reduced to <60 ppb) of the carbon dioxide (CO_2) in the sample.[79] The air stream is then split quantitatively into two streams, one of which passes through a converter that converts both the CO and the NMOC in that half of the air sample to CO_2. The second stream bypasses the converter. Downstream of the converter, the two streams are rejoined and pass through a chamber where optical absorption measurements are made by gas filter correlation of both the CO and the CO_2. Since the stream passing through the converter contains one-half the CO concentration and one-half the NMOC concentration in the original sample, and since the concentration of CO in the stream bypassing the converter is one-half that of the original sample, subtraction of CO from CO_2 gives a quantitative measure, when multiplied by 2, of the NMOC concentration in the sample. This approach appears highly advantageous, in that it would avoid all the problems associated with conventional NMOC methods.[14,78,79]

EPA is also investigating non-continuous gas chromatographic techniques in which samples are collected in inert bags and analyzed in a central laboratory using a cryogenic preconcentration procedure and a gas chromatograph with a special column designed to measure specific organic compounds. The chromatograph can be calibrated with specific individual compounds or a single compound, and total hydrocarbons can then be estimated as CH_4 by summing the response for all compounds of interest. In this approach, samples can be collected by less experienced personnel, stored, and later brought to the central laboratory for analysis. This technique is a simplified variation of the GC-mass spectrometry techniques often used to identify and measure specific organic compounds for developing and verifying some types of photochemical models.[14] Recent work has indicated the possibility of further simplifying the technique by eliminating the gas chromatographic column, selectively trapping the NMOC cryogenically, and passing the preconcentrated NMOC through the detector of the GC, so that a single response is obtained that is proportional to the NMOC concentration of the sample.[79] These methods would have the disadvantages of problems associated with storage of ambient air samples as described later in this section.

In addition to the above methods, more unique approaches for measuring NMOC have been proposed, including the chemiluminescence method for reactive hydrocarbons noted above and the use of chlorine atoms to abstract hydrogen atoms from organic molecules to form CO and CO_2. These approaches would require much further research, a redefinition of non-methane hydrocarbons, a determination of the relationship of these measurements to the photochemical formation of ozone, and possible modification or adaptation of the photochemical models.[12,14]

Though the more promising of the above methods are under development now, the research in progress represents a rather recent effort to refine and improve NMOC measurement methodology. The relatively slow development of NMOC methods can be attributed partly to the fact that the HC NAAQS, in keeping with its guideline nature, has never been enforced and compliance monitoring is not required under EPA regulations[4]. In part, however, the relatively slow development of NMOC methodology can be attributed to a lack of scientific consensus on how NMOC measurements should be defined or expressed.[12] Should they, for example, be related (1) to molar volume; (2) to mass; (3) to the product of carbon number and molar volume; or (4) to the product of molar volume and some reactivity factor?[12] Research on NMOC methodology will continue since there exists a demonstrated need for reliable and accurate, as well as inexpensive, field instrumentation for measuring total NMOC in ambient air and in source emissions.[80,81] Measurements of NMOC in ambient air are needed for diverse applications such as (1) analysis of trends in ozone air quality versus precursor ambient air levels, to determine the efficiency of control strategies; (2) verification of emission inventories by comparison with empirical data; (3) acquisition of input data for models used to determine reductions in hydrocarbon or volatile organic emissions needed to achieve and maintain the ozone standard; (4) acquisition of data required for the prediction of the impact of changes in the spatial configuration of sources, of the addition of major new sources, or of changes in temporal patterns of emissions; and (5) possible development of new or revised empirical models, since some empirical models may have been developed from NMOC measurements of doubtful quality.

Although there are numerous applications for which total NMOC are useful, there are also applications for which the detailed hydrocarbon composition, qualitative and quantitative, of ambient air must be known. Now, as in 1970, the only method available for compositional analysis of hydrocarbons in ambient air is gas chromatography (GC).[15,16] It is an accurate and reliable method, commercially available, for the measurement of individual hydrocarbons, NMHC, and total hydrocarbons.[73] With flame ionization detection, it is sensitive in the ppb range. With appropriate columns and temperatures, almost any desired separation of components can be achieved.[73] A number of factors, however, preclude the use of gas chromatography for the long-term, routine analysis of hydrocarbon mixtures in ambient air. First, the instrumentation and its operation are expensive. Second, the instrumentation is sophisticated and requires operator skill and experience. Third, data reduction is tedious and time-consuming. This problem, especially acute in 1971 when the NMHC Federal Reference Method was promulgated, has been alleviated by the development of automated systems that reduce, and often eliminate, the need for manual identification and calculation of the chromatogram peaks. These systems also permit automatic summation of individual hydrocarbon concentrations. In spite of these advances, however, the effort and personnel still needed for data reduction make this step expensive and time-consuming. Fourth, dynamic calibration with standards of individual hydrocarbons or hydrocarbon mixtures is required. When unknowns are encountered, or when resolution of peaks is poor, GC analysis must be supplemented with infrared or mass spectrometry for final identification.[73]

Though calibration and the need for supplementation by spectrometry are hindrances to the routine use of GC techniques, they also constitute part of the overall specificity of GC methods that is advantageous in detailed hydrocarbon analysis. Dynamic calibration with known compounds or mixtures means that quantitative evaluation of individual chromatogram peaks can be made without standardization of each compound peak. The concentration of each component can be computed by using an average per-carbon factor determined from measurements of known concentrations of the identified components.[82] The fact that GC techniques can be coupled with spectrometric techniques ensures the confirmation of compound identity; spectrometric techniques in and of themselves are imprecise for the determination of compounds in a mixture, but coupled with GC they become valuable in the final identification of organic compounds. An additional advantage of GC techniques is their sensitivity at the ppb level. In urban atmospheres, hydrocarbons generally exist at levels high enough to permit the collection and analysis of samples without pre-concentration. For analysis for rural air samples, in which hydrocarbons are typically present in parts-per-billion quantities or fractions therof, cryogenic trapping techniques are available for the pre-concentration of large samples.

An additional problem exists that complicates the use of gas chromatography--sampling procedures even for short-term studies. As yet, no material has been found that is ideal for use in fabricating air sample containers. Flexible bags made of Tedlar and Teflon are often used for sample collection and storage, but these materials result in some hydrocarbon losses and some contamination by bag emissions. Tedlar bags have been shown to be adequate for the storage of paraffinic and olefinic hydrocarbons (0.0 to 0.3 ppm C) for up to 191 hours. Aromatic hydrocarbons showed a 5 to 15 percent decay over this period.[83] Storage of zero-hydrocarbon air in Tedlar bags for 4 hours, however, resulted in production of up to 40 ppb C. Longer storage--24 to 48 hours--resulted in acetaldehyde and acetone in excess of that level. Irradiation prior to use increases emissions from Tedlar bags.[83] When zero air was stored, in another study,[84] in 5 mil Teflon bags, contamination of 1 ppm C occurred after 72 hours. The major contaminants of samples stored in Teflon have been identified as C_2-C_4 fluorinated hydrocarbons. Pre-irradiation for 12 hours and vacuum heating reduce contamination from Teflon outgassing but also reduce bag life. Untreated 2 mil Teflon produces no contamination by C_2-C_4 fluorinated hydrocarbons but does produce fluorinated aromatics with time.[84]

Stainless steel canisters have also been used in collection and storage of air samples for subsequent GC analysis. While they do not produce outgassing, canisters must be thoroughly cleaned after storage of each sample to prevent cross-contamination. Cleaning, however, often results in rust. Contamination from stainless steel canisters appears to be less severe than from Teflon or Tedlar bags. Because of the bulk, weight, and need for cleaning, canisters have not been favored as storage vessels by researchers in the field.[85]

Despite these sample handling and storage problems, gas chromatography can be an accurate method of analysis of individual hydrocarbons. Data presented later in this section, for example, were obtained by deploying mobile laboratories outfitted with gas chromatographs so that samples could be analyzed soon after they were obtained. Care was taken in these studies to identify any chromatogram peak artifacts so that they could be assigned to bag emissions rather than ambient air compounds.[84] Furthermore, analysis of hydrocarbon mixtures in ambient air must be performed by GC if the contributions of those mixtures and their individual components to photochemical oxidant formation are to be determined, and if relative contributions of various souces are to be evaluated.[86] Thus, for these and other applications in which compositional analysis is required, GC techniques must be used. Likewise, for short-term studies, such as may be required to provide data for use in a model or to validate a model over a short but intensive period of data collection, GC may not be too expensive and time-consuming but may, in fact, prove to be the method of choice.

6.3 SOURCES AND EMISSIONS OF HYDROCARBONS

6.3.1 General

Data on sources and emissions of hydrocarbons that appeared in the 1970 criteria document were for 1968. The most recent compilation of emissions data, prepared by EPA, covers 1977 but also includes summaries of data for 1970 through 1977. The data appearing in the 1970 document, as well as the more recent data, are not specific for hydrocarbons but include emissions of all volatile organic compounds (VOC). Consequently, most manmade emissions reported in this section will be referred to as VOC. Generally, emissions of methane, ethane, methyl chloroform, and Freon 112 are considered to have negligible photochemical reactivity and are not included.[73] For many stationary fuel combustion sources, however, sufficient information is not available to permit exclusion of these compounds, and current emission factors that include methane and ethane have been used to estimate these emissions. Highway vehicle emissions, which are reported as nonmethane hydrocarbons, are derived by subtracting methane from total hydrocarbon emissions.[87]

A summary of national emission estimates for VOC for 1970 through 1977 is presented in Table 6-3, and emissions of VOC by source category for 1977 are presented in Table 6-4.[88] It is clear from Table 6-4 that transportation is a major source of emissions. Other major sources of VOC emissions are industrial processes and miscellaneous sources. Within these two categories, chemical manufacturing (listed as chemicals), industrial organic solvent use, and miscellaneous organic solvent use (domestic and commercial) together total 9.1 x 10^6 MT/yr, nearly the total of VOC emissions produced by highway vehicles (9.9 x 10^6 MT/yr).

A very rough estimate of the percentage of VOC which are actually hydrocarbons may be obtained from Table 6-4 by assuming that emissions from chemical manufacturing and from industrial and miscellaneous organic solvent use are 100 percent non-hydrocarbon VOC. While this assumption is not wholly accurate, it is also true that exceptions to it are more than likely offset by non-hydrocarbon VOC emissions such as oxygenated or possibly even halogenated HC from highway vehicles, stationary source fuel combustion, oil and gas production and marketing, and miscellaneous combustion sources.

Evaporative VOC emissions result primarily from the transportation and storage of crude oil and volatile petroleum products such as gasoline and distillate fuel oil, and from the use of organic solvents for surface coating, degreasing, and other applications. Evaporative emissions from stationary sources have shown a steady increase over the years because of increased demands for motor vehicle fuels and organic solvents.[89] As the result of

TABLE 6-3. SUMMARY OF NATIONAL ESTIMATES OF VOLATILE ORGANIC EMISSIONS, 1970-1977[67]

(10^6 MT/yr)

YEAR	VOC
1970	29.5
1971	29.1
1972	29.6
1973	29.7
1974	28.6
1975	26.9
1976	28.7
1977	28.3

TABLE 6-4. NATIONAL ESTIMATES OF VOLATILE ORGANIC EMISSIONS, 1977, BY SOURCE CATEGORY[67]
(10^6 MT/yr)

Source category	VOC	% of Total
Transportation	11.5	41
Highway vehicles	(9.9)	
Nonhighway vehicles	(1.6)	
Stationary fuel combustion	1.5	5
Electric utilities	(0.1)	
Industrial	(1.3)	
Residential, commercial, and institutional	(0.1)	
Industrial processes	10.1	36
Chemicals	(2.7)	
Petroleum refining	(1.1)	
Metals	(0.1)	
Mineral products	(0.1)	
Oil and gas production and marketing	(3.1)	
Industrial organic solvent use	(2.7)	
Other processes	(0.3)	
Solid waste	0.7	2
Miscellaneous	4.6	16
Forest wildfires	(0.7)	
Agricultural burning	(0.1)	
Coal refuse burning	(0)[a]	
Structural fires	(0)	
Miscellaneous organic solvent use	(3.7)	
	28.3	100

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[a] Zero indicates emissions <50,000 MT/yr.

industrial growth, industrial process emissions have increased by about 17 percent. This increase has been offset by decreases in emissions from other categories. Emissions from highway vehicles have decreased as a result of emission control efforts by auto manufacturers in response to a Federal mandate, implemented under the Federal Motor Vehicle Control Program, for meeting requirements of Title II provisions of the Clean Air Act. This decrease of about 7 percent from 1970 through 1977 occurred in spite of an estimated 30 percent increase in motor vehicle travel during that period (see Section 6.3.3.2). Less solid waste was burned during that time, resulting in fewer emissions. Emissions from miscellaneous organic solvent use decreased as water-based emulsified asphalts were introduced in place of paving asphalts liquefied with petroleum distillates that evaporate when the asphalt cures. Overall, emissions of VOC decreased slightly from 1970 through 1977.

Emissions of VOC are not uniformly distributed throughout the United States. Figures 6-1 and 6-2, which are population density and VOC emission density maps prepared from 1975 data,[90,91] are presented to illustrate graphically the correspondence between population and pollution. The areas with the greatest population and greatest VOC emission densities are (1) the northeast corridor extending from Washington, D.C., to Boston; (2) certain industrial states (Illinois, Indiana, Ohio, Pennsylvania, and New York); and (3) states along the Gulf Coast. Maps showing VOC emission densities by county rather than state have better resolution.[88] These show that high emission densities also exist in the Los Angeles and San Diego, California, areas; and in portions of Texas and the Gulf Coast states.

Total emission inventories for the entire nation give no indication of the contributions of specific sources to local or regional ambient air

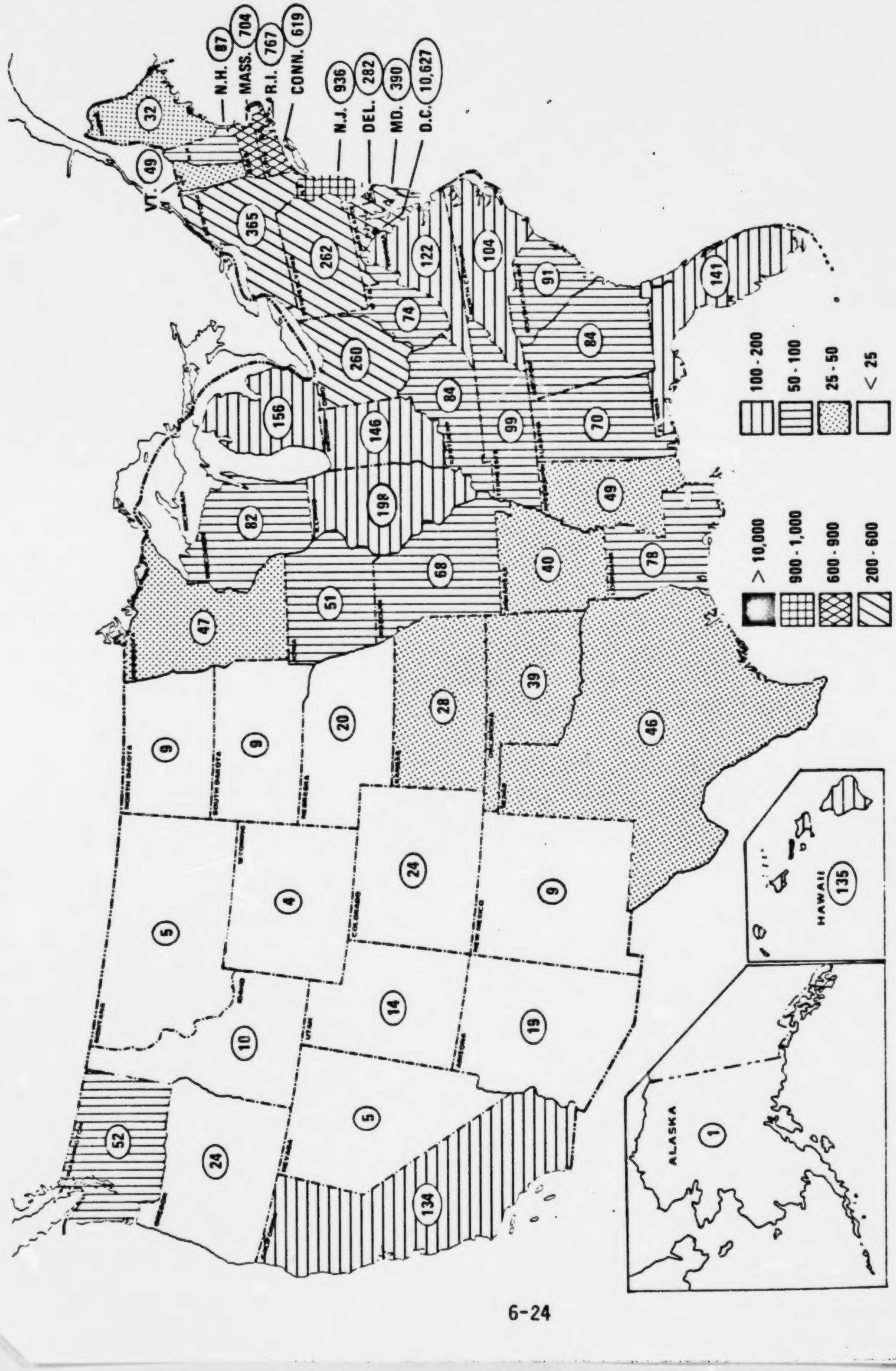
> 10,000
900 - 1,000
600 - 900
200 - 600
100 - 200
50 - 100
25 - 50
< 25
VT. 49
N.H. 87
MASS. 704
R.I. 767
CONN. 619
N.J. 936
DEL. 282
MD. 390
D.C. 10,627
32
365
262
122
104
91
141
74
260
84
84
156
146
99
70
82
198
49
47
51
68
40
78
9
9
20
28
39
46
5
4
24
9
10
14
19
52
24
5
134
ALASKA
1
HAWAII
135

Figure 6-1. Density of population in U.S. in 1975 by state, no. people/mi.[90,91]

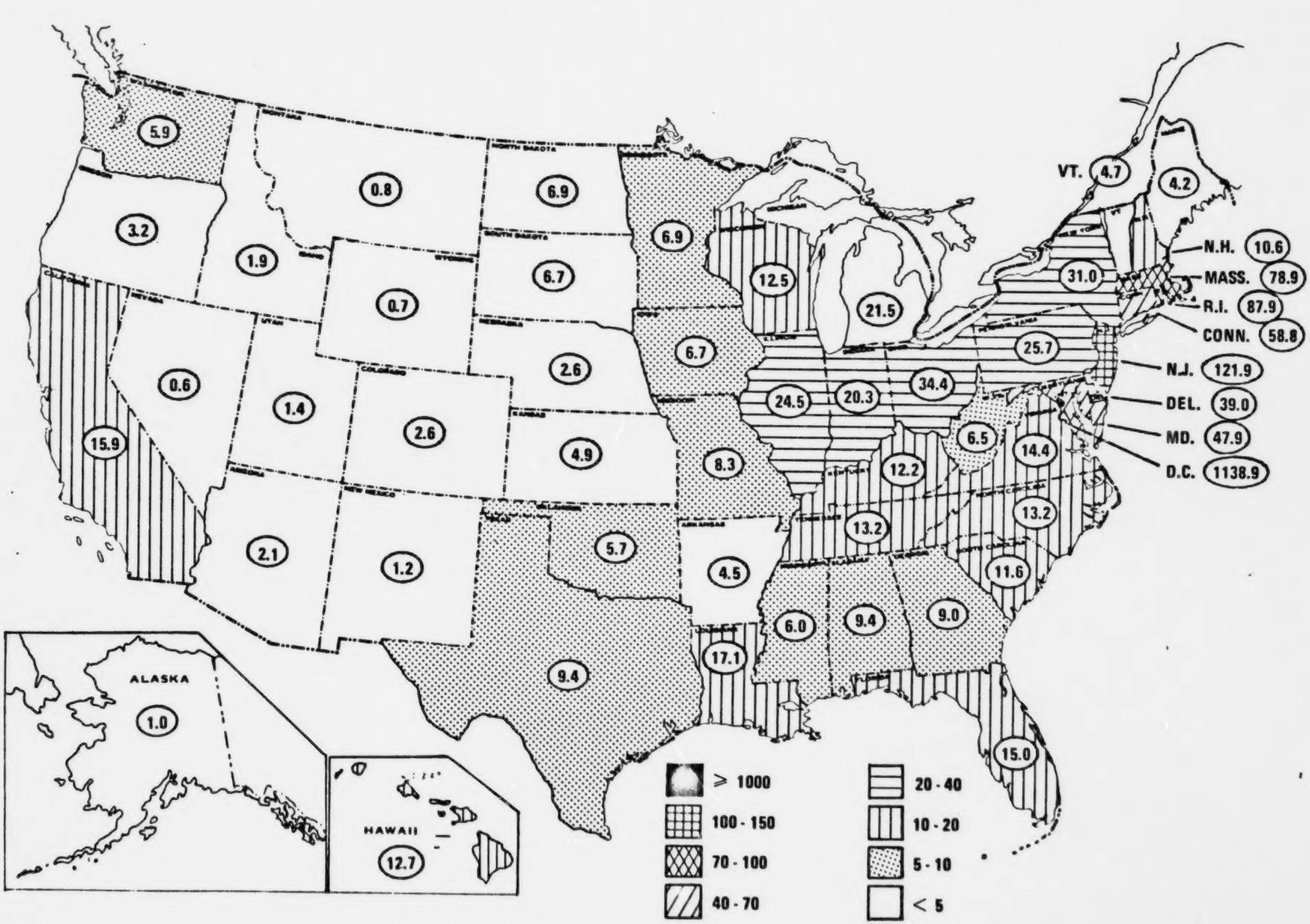
VT. 4.7
4.2
N.H. 10.6
MASS. 78.9
R.I. 87.9
CONN. 58.8
N.J. 121.9
DEL. 39.0
MD. 47.9
D.C. 1138.9
5.9
3.2
15.9
0.6
1.9
0.8
0.7
1.4
2.6
2.1
1.2
6.9
6.7
2.6
4.9
5.7
9.4
6.9
6.7
8.3
4.5
17.1
12.5
21.5
24.5
20.3
34.4
6.5
25.7
31.0
12.2
14.4
13.2
13.2
11.6
6.0
9.4
9.0
15.0
ALASKA
1.0
HAWAII
12.7
≥ 1000
100 - 150
70 - 100
40 - 70
20 - 40
10 - 20
5 - 10
< 5

Figure 6.2 Density of total nonmethane hydrocarbon emissions in U.S. in 1975 by state, tons/mi^2.[90,91]

concentrations of hydrocarbons. Local and statewide emission inventories give approximate indications of the contributions of respective source types, or categories, to the hydrocarbon loading in ambient air. The development of accurate and comprehensive emission inventories, however, is complicated by a number of factors, including shortcomings in emission measurement methodology (for determination of both composition of emissions and emission rates); lack of data on process emissions; inability to quantify manmade fugitive emissions; difficulties in identifying and quantifying natural emissions; and difficulties in estimating actual vehicle density, speeds, and miles traveled for mobile sources. Furthermore, atmospheric chemical reactions involving hydrocarbons and meteorological factors affecting their dispersion are quite complex, so that significant differences can exist between emission profiles and ambient air profiles, as demonstrated by Gordon et al.,[47] even if emission inventories are reasonably comprehensive and accurate. As a result, the contributions of respective sources to the ambient air concentrations of nonmethane hydrocarbons are not readily apparent nor easily determined.

A number of researchers have pioneered in the development of numerical techniques that can be used in conjunction with ambient air measurements to determine contributions from major source categories. In the case of aerosols, for example, the chemical element balance (CEB) technique of Friedlander,[62] which is based on material balance principles and on the fact that air pollution sources of a given type emit chemical elements in a characteristic, reasonably fixed proportion, can be used to determine the relative contributions of respective sources to ambient air aerosol mass. In this technique, if the emission sources in a given region are known, contributions to ambient air concentrations of particulate matter from those sources can be estimated by measuring the elemental concentrations at a given point and then solving a set of simultaneous linear equations. This technique has been applied fairly extensively to the estimation of source contributions to particulate matter.[92-95]

Similar numerical techniques can be used to calculate estimates of source contributions to the concentrations of vapor-phase hydrocarbons in ambient air. In this case, composition profiles, both qualitative and quantitative, of nonmethane hydrocarbons from major emission sources have been compiled and compared with ambient air profiles of NMHC by many investigators.[96-104]

Neligan[96] analyzed air samples in Los Angeles for detailed hydrocarbon composition in 1962. His comparison of ambient air profiles with the hydrocarbon composition of auto exhaust led to the identification of other sources of paraffinic hydrocarbons; namely, natural gas leaks, gasoline evaporation, and industrial emissions. From their study of Los Angeles air samples, Altshuller and Bellar[44] reported ambient air concentrations of ethane, propane, and isobutane that were five to ten times greater than the concentrations of these same compounds in auto exhaust given off during dynamometer studies. A comparison by Stephens and Burleson[97] of C_2-C_6 aliphatic hydrocarbons in ambient air in Riverside, California, to NMHC profiles for auto exhaust, liquid gasoline, gasoline vapor, and natural gas showed that propane probably originated from a combination of vehicular emissions, gasoline evaporation, and losses from natural gas and oil fields. High concentrations of ethane were found and attributed to natural gas sources. The results of that study also confirmed the finding of Altshuller and Bellar[44] that large amounts of propane occur in Los Angeles ambient air relative to the negligible amounts found in auto exhaust. It also confirmed the earlier work of Gordon et al.,[47] who had demonstrated that significant differences existed between ambient air hydrocarbon profiles and those of auto exhaust.

Lonneman et al.[98] studied auto emissions in the Lincoln Tunnel (New York City) in order to determine typical hydrocarbon profiles from autos under actual roadway, as opposed to dynamometer, operation. In this study, acetylene was used, because of its virtual nonreactivity, to normalize concentrations of all other nonmethane hydrocarbons. Ratios of ethylene, isobutane, n-butane, isopentane, and n-pentane to acetylene, as well as other NMHC/acetylene ratios, were derived for vehicular emissions. These ratios have since been confirmed, within experimental error, in a tunnel study in Houston.[99] The work of Kopczynski et al.[100] in St. Louis added to the species and ratios known to be indicative of automative-related sources. These workers found that o-xylene, ethylene, and 2-methylpentane, along with carbon monoxide and acetylene, occur in consistent proportions to other compounds. These compounds are all more reactive than acetylene, however, and losses will occur from photochemical reactions. Using the NMHC/acetylene ratio for vehicular emissions, Kopczynski et al.[100] estimated that less than 50 percent of the paraffinic and aromatic hydrocarbons in ambient air in St. Louis were attributable to automotive-related emissions; whereas most of the olefins in evening and early morning samples were automotive-related.

In the mid-1970s, Mayrsohn and Crabtree[101] developed a procedure, which they termed "source reconciliation," for estimating the relative contributions of respective sources to ambient air concentrations of hydrocarbons. Their procedure is a multivariate regression analysis which employs an algorithm, the logical and mathematical bases of which are too detailed to present here, to find normalization constants which correspond to the most accurate source configuration relative to an atmospheric hydrocarbon profile. The optimum source configuration results when the error between the normalized source component sums and the corresponding profile components is minimized. Source profiles were developed for major sources of atmospheric NMHC in the Los Angeles area and atmospheric profiles were determined from compositional analyses on ambient air samples collected at three sites in the area during the summer of 1973. The average distribution of NMHC according to source was estimated to be: automotive exhaust, 47 percent; gasoline (including liquid and vapor), 31 percent; commercial natural gas, 8 percent; and geogenic natural gas, 14 percent. If exhaust and gasoline are combined, automotive-related sources contributed about 78 percent of the C_2-C_{10} NMHC in ambient air in the Los Angeles area in 1973.

In a subsequent study covering June through September 1974, Mayrsohn et al.[102] applied their source reconciliation procedures to 900 NMHC analyses of samples obtained at eight sampling sites, seven of which were located on an east-west line extending from Los Angeles to Palm Springs, a distance of about 110 km (about 69 miles). The results of that study showed the estimated source contributions to ambient air NMHC (C_2-C_{10}) to be: automotive exhaust, 53 percent; gasoline, 12 percent; gasoline vapor, 10 percent; commercial natural gas, 5 percent; geogenic natural gas, 19 percent; and liquified petroleum gas, 1 percent. Again, when exhaust, gasoline, and gasoline vapor are combined, automotive-related sources contributed about 75 percent of the C_2-C_{10} NMHC in ambient air in the Los Angeles area in 1974. According to Mayrsohn et al.[102] the estimated source distribution obtained by their procedure differed substantially from the emissions inventory compiled for Los Angeles County, in which automotive exhaust was reported to account for about 90 percent of the mass of "reactive" hydrocarbons, a percentage that was determined by assuming a set of source composition and emission rate factors for sources of photochemically reactive hydrocarbons only.

From a preliminary source reconciliation study in Houston, Siddiqi and Worley[99] concluded that both automotive and industrial sources are important contributors to ambient air NMHC in Houston but that in downtown Houston automotive sources play the more important role. These researchers normalized concentrations of NMHC with the sum of acetylene plus propane, instead of acetylene only, as used by previous investigators,[98,99] because both are unreactive and the two could not be resolved on the gas chromatographic (GC) column used. Crabtree and Mayrsohn[103] later noted that if the unresolved acetylene-propane GC peak was due mostly to propane, instead of acetylene as assumed by Siddiqi and Worley,[99] then geogenic natural gas could well be the greater contributor to the NMHC burden in downtown Houston. Adding to this interpretation is the fact that Siddiqi and Worley found negligible hydrocarbons in the C_6-C_{10} range and nearly half of the mass of auto exhaust hydrocarbons is in this range.[98]

Seila[104] studied NMHC concentrations, composition, and source contributions in ambient air samples taken in January 1978 in Jones State Forest, about 61 km (38 miles) north of Houston. He found that automotive sources accounted for 35 percent and non-automotive sources for 54 percent of the NMHC burden in Jones State Forest samples. Of the non-automotive NMHC contribution, 41 percent was found to originate from sources in Houston and 59 percent from sources north of Houston. Most of the non-automotive NMHC contribution was attributed to refinery and natural gas emissions. Natural (vegetative) hydrocarbon emissions in these samples, all of which were taken within the forest, were reported to account for 2 percent of the NMHC loading.[104]

6.3.2 Natural Sources and Emissions

The estimates for VOC presented in the previous section included some natural VOC emissions, those given off by forest wildfires. Other natural sources of hydrocarbons (not VOC) have already been described in Section 5. The 1970 document cited Koyama's estimate[18] of natural methane emissions of 2.73×10^8 metric tons/yr (3×10^8 tons/yr). That estimate did not include methane emissions generated in swamps and tropical areas, and thus can be considered a conservative estimate. Robinson and Robbins[105] added production from swamps and humid tropical areas to Koyama's estimate for an estimated natural production of methane of 1.45×10^9 metric tons/yr (1.6×10^9 tons/yr). Assuming a methane emission rate per unit of land area that is half the world average--a reasonable assumption, given our temperate climate--natural methane emissions in the United States would be about 4.5×10^7 metric tons/yr (5×10^7 tons/year).[73] Though its role in photochemical smog systems is under renewed investigation,[106,107] methane is still considered to play little, if any, role in the photochemical formation of oxidants and other smog components.[7]

In addition to methane, other hydrocarbons are emitted from natural sources. A recent report by West German researchers[108] raises the possibility that natural benthic sources may be responsible for the occurrence of higher-molecular-weight, vapor-phase n-alkanes ($\geq C_9$) in "clean" ground-level air. They sampled air of three types in order to sort out the influence of manmade sources: (1) air influenced by passage over the European continent (surface winds and easterly trajectories); (2) clean marine air (no known recent contact with land masses as determined from trajectories); and (3) marine air influenced by passage over land areas, but predominantly influenced by passage over bodies of sea water. They also sampled sea water and surface films from sea water. They estimated the global oceanic strength of $\geq C_9$ vapor-phase n-alkanes to be 2 to 20 Tg/year (2×10^9 to 20×10^9 metric tons/yr). They concluded that it is unclear whether the bulk of n-alkanes observed in marine air originates from the sea surface or from the continents, but noted that the calculated residence times for the n-alkanes, which appear to be controlled by their reactions with $OH^{\cdot}$, are sufficiently short that only small quantities of higher continental n-alkanes should reach the open ocean. They did not rule out manmade fossil fuels, from spills and seepage, as the ultimate source, but did cite evidence for the production of n-alkanes by marine microorganisms.[108]

Vegetation is a well-known source of natural hydrocarbon emissions. It has been shown unequivocally that monoterpenes, C_{10} compounds with one to three double bonds, are emitted from evergreen foliage and that isoprene, a C_5 hemiterpene, a diolefin, is emitted from deciduous foliage.[19,109-114]

Rasmussen and Went[19] estimated a global production rate for volatile organics from vegetation of about 3.98×10^8 metric tons/yr (438×10^6 tons/yr). In more recent work, done since publication of the 1970 criteria document, Zimmerman estimated net worldwide emissions of all natural hydrocarbons, methane plus vegetational, at 7.54×10^8 metric tons/yr (8.3×10^8 tons/yr).[109] Zimmerman derived an estimate of isoprene plus terpene emissions of 6.36×10^7 metric tons/yr (70×10^6 tons/yr) in the United States.[115] The complexity of the factors involved, coupled with some methodological uncertainties, makes this estimate somewhat less than firm, but it appears to be the best estimate available for emissions from vegetation. The distribution of terpene and isoprene emissions is not as uniform in the United States as the methane emissions, based on background concentrations of methane measured at various sites. Zimmerman's emission inventory indicates that 43 percent of the total natural HC emissions occur during the summer months (June, July, and August); that 45 percent of the annual emissions occur in the southern United States, and that isoprene constitutes 34 percent of this portion.[115]

The role of natural hydrocarbon emissions in photochemical oxidant pollution is controversial, the controversy arising in large measure from apparent disparities between observed emission rates and aerometric data. Discussion of the issues is beyond the scope of this document, but detailed discussions are available in the open literature, including three recent EPA publications.[7,73,107,116-118] The role of natural hydrocarbons will again be addressed in detail in the next revision of *Air Quality Criteria for Ozone and Other Photochemical Oxidants*. This section merely presents a summary of the emission sources and rates for natural, vegetational hydrocarbons reported by various researchers. Aerometric measurements of natural hydrocarbons are presented in Section 6.4.

Using essentially the same techniques as those he used in making estimates of nationwide emissions of natural hydrocarbons, Zimmerman[119] conducted a study of natural hydrocarbons in Houston in 1978. He measured both emission rates and ambient air concentrations of isoprene and the monoterpenes at a large number of sites in the Houston area typical of various kinds of vegetation and typical of varying degrees of influence from manmade emissions. A summary of emission rates and ambient air measurements from this study is presented as Table 6-5.[119] Table 6-6 presents a comparison of emission rate data for Houston and the Tampa-St. Petersburg area, as reported by Zimmerman.[119]

TABLE 6-5. COMPARISON OF SELECTED HOUSTON EMISSION RATE AND AMBIENT AIR DATA[119]

Sample type	No. samples/ no. sites	Emission rate, μg/g/hr[a]	Ambient concentration, μg/m^3	Distance from branch, in.[b]
Live oak	12/2			
TNMHC		29.3	79.8	12
Isoprene		29.3	2.4	
Slash pine	6/1			
TNMHC		20	27.1	6
α-Pinene		5	1.5	
β-Pinene		4	0	
d-Limonene		7	0	
Slash pine	6/1			
TNMHC		0.5	43	6
α-Pinene		0.2	0	
β-Pinene		0.2	0	
Short leaf pine	1/1			
TNMHC		20	27	6
α-Pinene		5	1.5	
β-Pinene		4	0	
d-Limonene		7	0	
Common fig	1/1			
TNMHC		1	259	6
α-Pinene		0.1	1.3	
β-Pinene		0.1	2.4	
Red bay	1/1			
TNMHC		0.4	91	6
α-Pinene		0.1	4	
β-Pinene		0.3	0	

[a] Emission rate in μg/g of leaf biomass/hr.

[b] Distance at which grab samples were taken for ambient air measurements.

TABLE 6-6. COMPARISON OF HOUSTON AND TAMPA/ST. PETERSBURG TNMHC EMISSION RATES[119]

	Houston			Tampa/St. Petersburg		
Type	N	$\bar{X}$	sd	N	$\bar{X}$	sd
Oaks (daytime), µg/g/hr	7	26	23	47	23	23
Pines, µg/g/hr	7	5	7	70	9	11
NC-NI,[a] µg/g/hr	11	0.2	0.7	143	4	6
Soil, µg/m^2/hr	8	195	134	101	324	177
H_2O, µg/m^2/hr[b]	12	48	38	152	231	208

[a] NC-NI includes non-conifer trees and shrubs for which less than 50% of their TNMHC emission rate is isoprene (Non-Conifer, Non-Isoprene).

[b] Surface water measurements. Houston samples were taken from fresh, swamp, and ship channel surface waters.

The methods by which samples are taken for determination of natural HC emission rates are the subject of much of the current controversy over the role of natural HC in the atmosphere. Again, discussion of the methodologic assumptions and uncertainties is too detailed to be presented in this document. Basically, however, the Zimmerman method involves enclosing a branch of a tree or portion of other vegetation in a flexible plastic enclosure chamber in order to capture the vapor-phase organics emitted by the vegetation. Other methods have been used by other investigators to determine natural HC emission rates. Tingey,[120] for example, has used a glass chamber that encloses the entire plant. In the case of trees, seedlings are used.

Results obtained by Tingey for four isoprene producers and one terpene producer are shown in Table 6-7.[120] A comparison of emission rates for monoterpenes from various plant species is presented in Table 6-8, also taken from Tingey.[120]

Though technical details and arguments concerning the relative abundance of natural HC sources and emissions are not being presented in this document, it should be pointed out that a number of scientific techniques, facts, and questions are bound up in the present controversy over the contribution of natural HC to ambient air levels of total NMHC and to ozone formation. Uncertainties and room for error inhere in methods for determining emission rates; in methods for determining leaf biomass over areas even as large as a few square kilometers, not to mention entire areas of the country or the country as a whole;[121] in ambient air measurements--both sampling and analytical techniques--of natural HC; in models used to reconcile emissions and ambient air measurements; and in methods for establishing accurate inventories of manmade emissions of HC, such that the component of total NMHC in ambient air that is attributable to manmade emissions can be known with a verifiable degree of certainty. For further discussion of the various factors that are pertinent to the abundance and role of natural hydrocarbons, the reader is referred to a recent summary by Dimitriades[107] of issues regarding natural hydrocarbons and to a recent EPA publication.[73]

TABLE 6-7. BIOGENIC HC EMISSION RATES AT CONSTANT ENVIRONMENTAL CONDITIONS[a,120]

Plant species	Emission rate μg C/dm²/hr[b]	 μg C/g/hr[b]
Isoprene		
American sycamore	49.4	
Live oak	41.2	34.2
Soybean	0.007	-
Bush bean	0.010	-
Total monoterpenes		
Slash pine	-	6.4

[a] Leaf temperature was 30°C and light intensity was 800 μE/m²/sec.

[b] Generally calculated as emissions per unit of leaf surface of deciduous foilage; calculated as emissions per g of biomass for conifer needles.

TABLE 6-8. COMPARISON OF MONOTERPENE EMISSIONS FROM VARIOUS PLANT SPECIES[120]

	Emission rate		
Plant species	µg/g/hr	µg/m^2/min	Reference[a]
Slash pine			
Total monoterpenes	6.4	-	Tingey et al., 1980
α-Pinene	3.2	35.0	
Slash pine			
Total monoterpenes	2.6	-	Zimmerman, 1979
Loblobby pine			
α-Pinene	-	46.1	Arnts et al., 1978
Longleaf pine			
Total monoterpenes	5.6	-	Zimmerman, 1979
Cryptomeria (Japan cedar)			
Total monoterpenes	3.0	-	Kamiyama et al., 1978
Salvia (sage)			
Total monoterpenes	-	18.1	Tyson et al., 1974

[a] Complete citations given in Reference.[120]

6.3.3 Manmade Sources and Emissions

Several comprehensive descriptions of manmade sources and emissions of VOC are available.[10,122,123] EPA has published and periodically updates detailed, comprehensive data on VOC emission rates in Compilation of Emission Factors (AP-42), but because that document presents emission rates for source categories and subcategories in terms of total VOC rather than species of VOC or HC, the information given here was derived from two other EPA documents[122,123] and from Vapor-Phase Organic Pollutants,[10] published by the National Academy of Sciences.

6.3.3.1 Stationary Source Emissions--The material presented in this section was taken directly from or derived from Volatile Organic Compound (VOC) Species Data Manual,[123] a report prepared for EPA in 1978. The manual summarizes and documents the available information on species of VOC emitted from stationary and mobile sources in a format usable by those preparing emission inventories for photochemical models. Most of the information in the manual was obtained from material prepared for the California Air Resources Board or from reports supplied by EPA. Individual references will not be cited in the summary presented here, but are available in Reference 123.

The information summarized here was chosen to represent the kinds of emissions and sources characteristic of the major stationary source categories presented in Table 6-4: (1) stationary fuel combustion, (2) industrial processes, (3) solid waste disposal, and (4) miscellaneous sources.

Sources of stationary fuel combustion include both external combustion sources and internal combustion engines. The major fuels burned by external combustion sources are coal, oil, and natural gas. External combustion units include utility, industrial, commercial, and institutional boilers; commercial and domestic combustion units; process heaters; furnaces; kilns; etc. If units are properly operated and maintained, emissions from these sources are small. For example, a 1000 megawatt power plant is estimated to emit about 91 to 182 metric tons per year (100 to 200 tons per year) of volatile organic compounds.[124] This low concentration of organics in source effluents makes their analysis difficult and readily accounts for the fact that newer information,[122,123] based on newer and more sophisticated technologies, may disagree with emission rates and species presented in the NAS document,[10] which were based on 1968 data. Table 6-9 presents a profile of the VOC emitted from external combustion sources, categorized by fuel burned.

Internal combustion engines are used in applications similar to those employing external combustion units. Internal combustion engines may be turbines or reciprocating engines, and may be fueled by the usual fossil fuels such as diesel, oil, or natural gas. They are used in electrial power generation, in gas pipeline pump and compressor drives, and in various industrial processes. The majority of gas turbines are used in electrical generation for continuous, peaking, or stand-by power. Table 6-10 tabulates emissions of VOC from internal combustion engines used in electrical power generation and in industrial processes. Note the differing emission profiles for larger versus smaller (30 hp) reciprocating engines. Smaller engines also have higher emission rates (emissions per unit of fuel burned) than larger engines, though the profiles presented here do not include comparisons of emission rates.

TABLE 6-9. EMISSIONS OF VOLATILE ORGANIC COMPOUNDS FROM STATIONARY EXTERNAL COMBUSTION SOURCES[123]

(wt %)

	Fuel				
Compound emitted	Residual oil	Distillate oil	Natural gas	Refinery oil	Coke oven gas
Methane	11.0	-	56.0	7.6	82.8
Formaldehyde	42.0	48.7	8.0	7.6	-
Ethane	-	-	-	20.9	2.5
Ethylene	-	-	-	-	11.7
Acetylene	-	-	-	-	0.8
Acetone	28.0	-	-	-	-
Propane	-	1.2	4.0	18.9	-
Propylene	-	-	-	17.5	0.3
n-Butane	14.0	12.2	9.0	23.1	-
Isobutane	-	4.1	-	4.4	-
n-Pentane	-	4.7	6.0	-	-
Isomers of pentane	-	5.5	9.0	-	-
n-Hexane	5.0	10.8	-	-	-
Isomers of hexane	-	5.2	1.0	-	-
n-Heptane	-	0.3	-	-	-
Isomers of heptane	-	2.6	-	-	-
n-Octane	-	-	-	-	-
Isomers of octane	-	4.7	-	-	-
Cyclohexane	-	-	1.0	-	-
Benzene	-	-	4.0	-	1.9
Toluene	-	-	2.0	-	-

TABLE 6-10. EMISSIONS OF VOLATILE ORGANIC COMPOUNDS FROM STATIONARY SOURCE INTERNAL COMBUSTION ENGINES[74]
(wt %)

Compound emitted	Electrical generation: Natural gas, turbine	Electrical generation: Diesel, recip.	Industrial: Dist. oil, recip.	Industrial: Natural gas, recip.	Industrial: Natural gas, recip. (30 hp)
Methane	70.0	11.6	11.6	76.0	93.5
Formaldehyde	30.0	-	-	1.0	-
Ethane	-	2.8	2.8	10.0	2.6
Ethylene	-	28.7	28.7	1.0	2.5
Acetylene	-	11.3	11.3	-	0.9
Propane	-	-	-	10.0	0.4
Propylene	-	17.3	17.3	-	0.1
n-Butane	-	-	-	1.0	-
Isobutane	-	-	-	1.0	-
Butene	-	13.4	13.4	-	-
1,3-Butadiene	-	7.0	7.0	-	-
Benzene	-	7.9	7.9	-	-

The manufacture of chemicals and chemical-based products contributes about 27 percent of the total VOC emissions attributable to industrial processes (Table 6-4). Emissions from the manufacture of one chemical and two chemical-based products are shown in Table 6-11. As demonstrated in this table and from comparison of this table with the preceding tables, emissions from chemical manufacturing show wide qualitative variations. No one organic compound or group of compounds dominates emissions.[10]

In the case of varnish manufacture, cooking and thinning operations are the major sources of VOC emissions. Incineration and catalytic oxidation have been used to control VOC from varnish-making; 99 percent control is possible with incineration. Uncontrolled emissions of VOC are about 185 kg/MT of product, but controlled emissions are about 1.85 kg/MT.

Phthalic anhydride is produced by the vapor-phase oxidation of naphthalene or o-xylene with excess air or catalysis. Reactor and condensor effluents are the main sources of VOC emissions, but other, minor sources are present. The emissions profile in Table 6-11 for phthalic anhydride production is a composite of all sources.

Printing inks consist of a fine dispersion of pigments or dyes in a vehicle that consists of a drying oil with or without resins and added driers or thinners. The preparation of the vehicle, by heating, is the largest source of VOC from ink manufacturing. Composite controlled emissions from ink manufacturing, reduced by about 90 percent of uncontrolled by means of scrubbers or condensers followed by an afterburner, are about 21 kg/MT of product.

Though the disposal of solid wastes contributes only 2 to 3 percent of all VOC emissions in the United States, Table 6-12, a profile of VOC from

TABLE 6-11. EMISSIONS OF VOLATILE ORGANIC COMPOUNDS FROM MANUFACTURE OF SELECTED CHEMICALS/PRODUCTS (wt %)

Compound emitted	Varnish	Phthalic anhydride[a]	Printing inks
Methane	-	80.0	-
Methyl alcohol	-	-	5.0
Ethane	-	0.4	-
Ethyl alcohol	-	-	2.5
Acetone	38.7	8.6	5.5
Glycol ether	3.0	-	-
Acetylene	-	4.4	-
Propane	-	11.7	-
Isopropyl alcohol	-	-	38.0
Methyl ethyl ketone	41.6	-	5.0
Propylene	-	3.1	-
n-Butane	-	36.1	-
Isobutane	-	0.4	-
n-Butyl alcohol	-	-	3.0
n-Butyl acetate	-	-	4.0
Methyl isobutyl ketone	16.7	-	-
Isomers of pentane	-	22.6	-
n-Hexane	-	21.4	-
Cyclohexane	-	11.3	5.0
Ethylbenzene	-	-	3.0
Isomers of diethylbenzene	-	-	3.5
Mineral spirits (paraffins)	-	-	25.5

[a] Composite emissions from chemical wastes.

TABLE 6-12. EMISSIONS OF VOLATILE ORGANIC COMPOUNDS FROM SANITARY LANDFILLS

Compound emitted	Wt %
Methane	98.6
Ethane	0.1
Perchloroethylene	0.3
Propane	0.1
_n_-Butane	0.2
Isobutane	0.1
_n_-Pentane	0.1
Cyclopentane	0.2
Terpenes	0.1
Toluene	0.1
Isomers of xylene	0.1

sanitary landfills, is included here as an indication of the kinds of emissions that are given off from solid wastes. The use of sanitary landfills is a long-accepted method for the disposal of residential and industrial wastes, most of which consist of refuse, domestic garbage, and inert construction materials. Waste is generally layered, compacted, and covered by thin layers of silt. Consequently, anaerobiosis occurs, resulting in the generation of appreciable amounts of methane-rich gas. Methane and carbon dioxide together constitute about 99 percent of gaseous emissions from landfills.

Next to emissions from highway vehicles, miscellaneous use of organic solvents contributes the largest percentage of total VOC emissions in the United States, 13 percent. Three examples of area source emissions of VOC in this category are presented in Tables 6-13 through 6-15. Domestic solvents are those found in products used around the house, garage, or yard. Emissions of VOC from domestic chemicals or chemical-based products result from the vaporization of low-boiling-point solvents in the product, the quantity and species depending on the product. Composite estimates of the percentage by weight of organic species emitted from domestic solvents are given in Table 6-13; they were calculated on the basis of annual sales of products containing these solvents. Organic emissions from domestic chemical use are estimated at 1.0 metric tons/1000 people/yr (1.1 tons/1000 people/yr).

Pesticides are commonly available in the form of liquids, aerosols, or powders and are applied by spraying, or dusting, or both. The VOC emitted from pesticide use arise from vaporization of the pesticide itself or from the solvent(s) used as the pesticide vehicle. Table 6-14 presents a profile of VOC emissions resulting from the domestic and commercial use of pesticides.

TABLE 6-13. EMISSIONS OF VOLATILE ORGANIC COMPOUNDS FROM GENERAL USE OF DOMESTIC SOLVENTS[a]

Compound	Wt %
Formaldehyde	0.6
Ethyl alcohol	36.9
Acetone	1.4
Glycol ether	8.3
Propylene glycol	3.2
Isopropyl alcohol	38.5
Isobutane	5.3
_n_-Butyl acetate	1.3
Naphtha	4.5

[a] Estimated at 1.0 metric tons/1000 people/yr (1.1 tons/1000 people/yr). Many common domestic products contain solvents: furniture polish, shoe polish, shaving soap, perfumes, cosmetics, shampoo, hair spray, hand lotion, rubbing alcohol, nail polish remover, etc.

TABLE 6-14. EMISSIONS OF VOLATILE ORGANIC COMPOUNDS FROM DOMESTIC AND COMMERCIAL USE OF PESTICIDES[a,123]

Compound	Wt %
Methylene bromide	10.0
Propane	1.8
n-Butane	4.4
Isobutane	1.4
n-Pentane	3.2
Isomers of pentane	3.1
n-Hexane	3.7
Isomers of hexane	8.1
C_7 cycloparaffins	15.4
C_8 cycloparaffins	1.6
Mineral spirits (paraffins)	15.0
Benzene	12.3
Toluene	5.0
Isomers of xylene	15.0

[a] Estimated at 8.2 metric tons/100,000 people/yr (9 tons/100,000 people/yr).

Total VOC emissions from pesticide use have been estimated at 8.2 metric tons/1000,000 people/yr (9 tons/100,000 people/yr).

Table 6-15 presents a profile of VOC emissions resulting from the use of architectural coatings, which are those paints and other coatings applied to stationary surfaces such as pavements and curbs, and structures and their appurtenances. Industrial coatings are excluded from this table. When paints and other coatings are applied, the solvents in the coating materials must evaporate so that the coating can form a film or barrier. The evaporation of these solvents, along with that of the solvents used to thin coatings or to clean up, generate emissions that represent a significant area source of VOC emissions. Emissions of VOC from the use of paints and other coatings in Southern California were estimated to be 3.2 metric tons/1000 people (3.5 tons/1000 people) in 1976. Because solvent emissions are controlled in California (Rule 442, formerly Rule 66), this estimate is probably low relative to the rest of the country.

Finally, profiles are given for VOC emissions given off by forest fires and from the open burning of agricultural and landscape wastes such as spent field crops, weeds, prunings, etc. (Table 6-16). Ground-level open burning is affected by many variables, including wind, ambient temperature, composition and moisture content of the wastes, and compactness of the burning refuse. Likewise, emissions differ according to burning pattern, i.e., head fires or back fires. Actual emission rates are difficult to calculate because of the important influence of these variables and none were given for the profiles shown in Table 6-16. In a separate study on emissions from agricultural burning, Darley[125] determined speciation and emission factors for hydrocarbons and some aldehydes from the burning of residues of eight selected field and orchard crops: barley, corn, rice, sorghum, and wheat; and almond, grape, and peach (Table 6-17).

TABLE 6-15. EMISSIONS OF VOLATILE ORGANIC COMPOUNDS FROM THE USE OF ARCHITECTURAL SURFACE COATINGS[a],[123]

Compound	Wt %
Acetone	3.2
Methyl alcohol	3.9
Ethyl alcohol	0.6
Ethylene glycol	0.6
2-Ethoxyethyl acetate	1.3
Dimethylformamide	0.5
Isopropyl alcohol	16.4
Methyl ethyl ketone	5.6
Propylene glycol	0.8
n-Butyl alcohol	1.6
n-Butyl acetate	2.5
Isobutyl alcohol	0.6
Isobutyl acetate	1.5
Methyl *n*-butyl ketone	0.7
Methyl isobutyl ketone	0.6
Isobutyl isobutyrate	6.1
n-Hexane	20.7
Cyclohexane	20.7
Toluene	5.2
Isomers of xylene	2.6
Ethylbenzene	4.3

[a] Estimated at 3.2 metric tons/1000 people/yr (3.5 tons/1000 people/yr), but since estimates were derived from Southern California, which is subject to control of solvent vapors, this estimate is probably low.

TABLE 6-16. EMISSIONS OF VOLATILE ORGANIC COMPOUNDS FROM FOREST FIRES AND FROM OPEN BURNING OF AGRICULTURAL/LANDSCAPE WASTES (wt %)

Compound emitted	Forest fires	Agricultural/landscape burning
Methane	9.8	-
Ethane	10.5	-
Ethylene	19.1	19.4
Acetylene	8.4	1.9
Methyl acetylene	0.4	-
Propane	0.4	1.9
Propylene	3.9	-
_n_-Butane	0.2	1.9
Isobutane	0.1	1.9
Butene	-	5.9
Isomers of butene	0.8	-
1,3-Butadiene	0.5	-
3-Methyl-1-butene	0.2	-
_n_-Pentane	-	1.9
Isomers of pentane	0.2	-
1-Pentene	-	11.8
Isomers of pentene	-	11.8
_n_-Hexane	-	13.9
_n_-Heptane	-	13.9
_n_-Octane	-	13.8
Unidentified HCs	44.6	-

TABLE 6-17. HYDROCARBON EMISSIONS FROM AGRICULTURAL BURNING OF FIELD AND ORCHARD CROP RESIDUES[125]

Crop	Type of fire	Avg. emissions, lb THC/ton fuel	HC in air sample, %			
			Methane	Other saturates	Olefins	Acetylene
Barley	Head	18.8	49.3	14.1	33.0	3.7
	Back	12.5	53.3	5.7	34.2	6.8
Corn	Head	5.7	55.9	10.1	29.6	4.5
	Back	7.6	52.9	9.4	31.4	6.3
Rice	Head	2.8	54.2	6.5	33.0	6.4
	Back	2.8	50.1	6.5	35.8	6.9
Sorghum	Head	2.1	62.9	6.9	25.9	4.3
	Back	3.5	55.1	7.3	31.6	6.0
Wheat	Head	18.1	47.7	7.8	37.0	7.6
	Back	9.4	49.5	5.2	35.5	9.8
Almond	Pile	4.5	60.5	8.8	24.9	5.8
Grape	Pile	4.9	54.0	9.6	27.9	8.5
Peach	Pile	3.2	61.7	6.7	22.0	9.6
Average values						
Field crops		8.3	53.1	8.0	32.7	6.2
Orchard crops		4.2	58.7	8.4	24.9	24.9

Combustion and sampling took place in an outdoor, instrumented burning tower (an inverted funnel with a stack) that simulated open burning but channeled the combustion products so that representative samples of gases could be taken. Measurements for hydrocarbons in isokinetically sampled air were made with gas chromatography coupled with mass spectrometry. Hydrocarbons $> C_6$ were first absorbed in a charcoal canister, then desorbed and chromatographed. Aldehydes were determined as the respective 2,4-dinitrophenylhydrazones. Field crops were burned as head and back fires and orchard crops were burned in piles.

Most of the samples contained compounds up through cis-2-butene ($\leq C_4$); occasionally compounds through 1-pentene ($\leq C_5$) were found. Analytical problems were encountered in the determination of aromatics ($\geq C_6$), but benzene and toluene were detected from field crop combustion, by both laboratories doing the analyses, in both head and back fires. Benzene emissions were reported to be highest from barley head fires (0.364 kg/metric ton of fuel) [0.728 lb/ton of fuel] and lowest from sorghum head fires (0.014 kg/metric ton of fuel) [0.028 lb/ton of fuel]. Toluene emissions were highest from barley head fires [0.297 lb/ton of fuel] and lowest from sorghum (head fires, 0.005-0.01 kg/metric ton of fuel; back fires, 0.0015 kg/metric ton of fuel) [head fires, 0.001-0.020 lb/ton of fuel; back fires, 0.003 lb/ton of fuel].

Of the hydrocarbons $\leq C_6$, methane constituted more than half of the emissions from both field and orchard crops. Olefins constituted 32.7 and 24.9 percent of hydrocarbon emissions from field and orchard crops, respectively. Ethylene was the most abundant olefin, constituting 69.1 percent of olefinic emissions from both field and orchard crops.[125]

This survey of VOC species and their emissions demonstrates the diversity of compounds arising from various types of sources. It also serves to corroborate the estimate made earlier in this section that as much as 30 percent or more of VOC emissions may be non-hydrocarbons.

6.3.3.2 Mobile Source Emissions--Nationwide estimates of VOC from transportation sources are shown for 1970 through 1977 in Table 6-18.[88] As that table shows, emissions from highway vehicles decreased nearly 7 percent from 1970 through 1977.[88] This decrease was achieved in the face of an increase during that period of about 30 percent in vehicle miles traveled. The decrease resulted mainly from the application by auto manufacturers of a variety of control devices. Some decrease was undoubtedly effected, as well, through improved fuel economy such that the increase in vehicle miles traveled was not accompanied by an equivalent increase in fuel consumption and, hence,

TABLE 6-18. NATIONWIDE ESTIMATES OF VOC EMISSIONS FROM TRANSPORTATION SOURCES, 1970 THROUGH 1977[88]

Year	Total transportation VOC emissions, 10^6 MT/yr	Highway VOC, 10^6 MT/yr	% of total transportation emissions	Nonhighway VOC, 10^6 MT/yr	% of total transportation emissions
1970	12.2	10.6	86.9	1.6	13.1
1971	12.2	10.6	86.9	1.6	13.1
1972	12.5	10.9	87.2	1.6	12.8
1973	12.3	10.7	87.0	1.6	13.0
1974	11.5	10.0	87.0	1.5	13.0
1975	11.3	9.8	86.7	1.5	13.3
1976	11.6	10.0	86.2	1.6	13.8
1977	11.5	9.9	86.1	1.6	13.9

in exhaust emissions. As an example of the decreases in hydrocarbon emissions accomplished by vehicle manufacturers through the use of pollution control devices, exhaust hydrocarbon emission factors for gasoline-powered light-duty vehicles are shown in Table 6-19 for 1968 through 1980 model-year vehicles, by calendar year of operation.[126] Composite crankcase and evaporative hydrocarbon emission factors for the same period are given in Table 6-20.[127] Crankcase and evaporative emissions are, besides exhaust emissions, the main source of hydrocarbons from vehicles. Since crankcase emissions from post-1963 vehicles are negligible, emission factors are determined for crankcase and evaporative emissions together.[127] The main sources of evaporative emissions, as noted earlier in Section 5.3, are the fuel tank and the carburetor system. Crankcase and evaporative emissions may increase over the lifetime of the vehicle, but properly maintained control devices for these emissions are assumed not to deteriorate with age.[127] Representative pollution control devices developed by the auto industry to achieve hydrocarbon emission reductions are shown in Table 6-21;[127] while these are emission control systems used by General Motors, they indicate the basic kinds of systems employed by all U.S. auto manufacturers to meet Federally mandated emission standards.

A discussion of the calculation of emission estimates such as those presented in Table 6-18 is beyond the scope of this report. It should be noted, however, that the data base used and assumptions made in making those calculations render them complex. For example, the estimate of total VOC emissions attributable to transportation sources (Table 6-18) is derived from mobile source emission factors and vehicle miles traveled, both of which, in turn, are based on additional data such as factors for the deterioration with age of pollution control devices, the "mix" of kind and age of vehicles in

TABLE 6-19. HYDROCARBON EXHAUST EMISSION FACTORS[a,b] FOR LIGHT-DUTY, GASOLINE-POWERED VEHICLES FOR ALL AREAS EXCEPT CALIFORNIA AND HIGH-ALTITUDE[127]
(g/mi)

Model Year	July, calendar year of operation										
	1970	1971	1972	1973	1974	1975	1976	1977	1978	1979	1980
1968	4.3	5.0	5.7	6.3	6.9	7.4	7.9	8.3	8.7	9.1	9.4
1969	3.5	4.3	5.0	5.7	6.3	6.9	7.4	7.9	8.3	8.7	9.1
1970	2.7	3.5	4.3	5.0	5.7	6.3	6.9	7.4	7.9	8.3	8.7
1971		2.7	3.5	4.3	5.0	5.7	6.3	6.9	7.4	7.9	8.3
1972			2.7	3.5	4.3	5.0	5.7	6.3	6.9	7.4	7.9
1973				2.7	3.5	4.3	5.0	5.7	6.3	6.9	7.4
1974					2.7	3.5	4.3	5.0	5.7	6.3	6.9
1975						1.3	1.6	1.9	2.2	2.5	2.8
1976							1.3	1.6	1.9	2.2	2.5
1977								1.3	1.6	1.9	2.2
1978									1.3	1.6	1.9
1979										1.3	1.6
1980											0.3

[a] Emission factors for vehicles through model year 1975 and through calendar year 1975 are based on actual surveillance tests of in-use vehicles. Post 1975 calendar year factors for all model-year vehicles are projected. Deterioration factors used are: pre-1968, 0.58; 1968-1974,0.53; 1975-1979, 0.23; and ≥ 1980, 0.23 -- all in g/mi per 10,000 miles of travel. For complete information on the calculation of emission factors, see reference 127.

[b] To convert g/mi to g/km divide g/mi by 1.609.

TABLE 6-20. COMPOSITE CRANKCASE AND EVAPORATIVE EMISSION FACTORS FOR LIGHT-DUTY, GASOLINE-POWERED VEHICLES FOR ALL AREAS EXCEPT CALIFORNIA AND HIGH-ALTITUDE[127,a]
(g/mi)

Model year	Emissions
1968-1970	2.53
1971-1977	1.76
1978-1979	0.60
1980	0.15

[a] To convert g/mi to g/km divide g/mi by 1.609.

TABLE 6-21. GENERAL MOTORS CORPORATION SYSTEMS FOR CONTROL OF HYDROCARBON AND OTHER POLLUTANT EMISSIONS[128]

Control system	Year introduced		Description
	California	Other states	
1. Positive crankcase ventilation (PVC)	1961	1963	1. Controls crankcase HC emissions; control valve draws clean air through crankcase into manifold so that crankcase HC vapors are burned.
2. Air injection reaction (AIR, Pulsair)	1966		2. Draws air into engine exhaust system to promote oxidation of unburned fuel and carbon monoxide.
3. Controlled combustion system (CCS)	1966	1968	3. Alternative to AIR or Pulsair; reduces pollutants emitted by fuel (HC) combustion through: (1) optimization of basic engine; (2) use of carburetor air temperature control; (3) improvements in carburetor controls; and (4) improvements in spark timing controls. Net results are recalibration of air/fuel mixture and ignition timing and prewarming of intake air.
4. Evaporative controls	1970	1971	4. Controls fuel HC vapors. Charcoal canisters absorb HC vapors from fuel tank and carburetor; air drawn through canister when engine is running recirculates vapors to engine for burning.
5. Exhaust gas recirculation (EGR)	1972	1973	5. Controls NO_x. EGR system uses valves to recirculate exhaust gas, in relation to exhaust backpressure, to inlet manifold, where it is mixed with inlet charge. Exhaust acts as diluent which reduces combustion temperature, thus lowering NO_x emissions.

TABLE 6-21 (continued).

Control system	Year introduced		Description
	California	Other states	
6. Oxidizing catalytic converter	1975	1975	6. Promotes oxidation of HC and CO. Exhaust gases pass over catalyst, causing HC and CO to be oxidized, by excess O_2 in catalyst, to CO_2 and H_2O. Not efficient for NO_x reduction.
7. Computer-controlled catalytic converter (C_4)	1980	1981	7. Oxidizing-reducing catalytic converter. Promotes oxidation of HC and CO and reduction of NO_x to N_2 and O_2. Achieves this by instrumentation, including digital computer that maintains stoichiometric air/fuel (A/F) ratio. (Oxidation of HC and CO → CO_2 and H_2O requires stoichiometric A/F; reduction of $NO_x \rightarrow N_2$ and O_2 requires $\leq$ stoichiometric A/F.)

use, vehicle registration, fuel consumption, etc.[128] Thus, the stated decrease in transportation-related VOC emissions of about 7 percent from 1970 through 1977 may be greater if EPA has overestimated the deterioration with age of pollution control devices, and thus the VOC emissions from controlled cars, as has been claimed by the Motor Vehicle Manufacturers Association. For detailed discussion on that point, the reader is referred to the proceedings of an emission inventory/factor workshop sponsored by EPA in 1977,[129,130] and to documentation related to requests by auto manufacturers for waiver of the 1981 Federal emission standard for carbon monoxide from mobile sources.[131,132]

Though VOC emissions from highway vehicles decreased about 7 percent from 1970 through 1977 (Section 6.2.1), motor vehicles remain the largest single category of contributors to atmospheric HC burdens, and are the most influential widespread source of VOC emissions in general and of hydrocarbon emissions in particular. Stationary sources have a major impact in most urban areas and in some urban areas, such as Houston and Chicago, they may have greater impact than mobile sources.[133] Nevertheless, HC emissions from light-duty gasoline vehicles come the closest to being ubiquitous and consistent in composition of any hydrocarbon mixtures from any major sources. This section is limited mainly to a discussion of hydrocarbon and oxygenated hydrocarbon emissions from diesel- and gasoline-powered automobiles, since they are the most important mobile sources of gas-phase hydrocarbons. According to EPA data,[88] highway vehicles account for 86 to 87 percent of all transportation-related VOC emissions; and aircraft, railroads, marine vessels, and other non-highway vehicles together account for 13 to 14 percent.

The 1976 NAS document on vapor-phase organic pollutants states that gasoline-powered vehicles account for about 99 percent of all vehicular hydrocarbon emissions.[10] While this estimate is probably high now because of a growing trend toward use of diesel engines, it is still true that most cars and light-duty trucks are gasoline-powered.

As noted in Section 5.3, there are potentially four sources of volatile hydrocarbons and other organic compounds from gasoline-powered vehicles: crankcase blowby emissions, carburetor evaporative emissions, fuel tank evaporative emissions, and exhaust emissions. Diesel vehicles emit volatile hydrocarbons and other organic compounds almost exclusively from the exhaust; evaporative emissions are practically nonexistent because of low fuel volatility.[134,135]

Sources of vehicle emissions have come under increasing control since 1963 when the introduction of positive crankcase ventilation systems virtually eliminated blowby emissions from gasoline-powered vehicles. The introduction of absorption-regeneration systems in 1970, which reduce evaporative emissions, has resulted in a decline of more than 80 percent since that time in atmospheric emissions from carburetor and fuel tank evaporation.[136] Likewise, exhaust HC emissions have been reduced by about 90 percent in new vehicles since 1968 by means of a variety of engine modifications, including, most recently (about 1975), catalytic oxidation systems. The actual reduction in HC emissions effected by these control systems is less than the percentages cited above because of the inevitable deterioration of these control devices.[73] Nevertheless, with the implementation of these emission controls in highway vehicles, emissions from mobile sources have been reduced in spite of continuing increases in motor vehicle travel. As cars are replaced, both current control systems and more advanced controls anticipated for the future are expected to reduce HC emissions from motor vehicles further, at least up through the mid-to-late 1980s.[73] However, it is projected that the automobile will continue to be a significant source of air pollution, partly because of the expected continued concentration of automobiles in congested urban areas.[137]

For late-model cars equipped with catalytic oxidation systems, evaporative emissions account for nearly one-third to one-half of THC emissions; and exhaust emissions account for the rest.[138] Deterioration of exhaust control systems results in a change in those proportions with time, however, so that exhaust emissions from a car 4 to 5 years of age can be expected at that time to contribute the major fraction of vehicle hydrocarbon emissions.

Because of the contribution of evaporative emissions, it is worthwhile to look at the composition of gasoline and of gasoline vapor as well as the composition of exhaust emissions. Gasoline normally contains more than 200 hydrocarbon compounds, mainly in the C_4 to C_{10} range. Alkanes and aromatics generally constitute the largest fraction, but olefins and naphthenes are also present. Final gasoline composition is the result of the mixture of about six blending stocks. The highest octane blending components in gasoline are aromatics and branched-chain paraffins. Different gasoline blends are required for different climatic regions of the United States. A summary of gasoline composition data, for a composite blend that is representative of U.S. consumption, is given in Table 6-22.[139] The average composition of gasoline vapor, determined from weighted averages of gasoline blending stocks and vapor pressures of respective compounds, is shown in Table 6-23.[139]

TABLE 6-22. SUMMARY DATA ON GASOLINE COMPOSITION, REPORTED AS WEIGHT PERCENT[139]

Hydrocarbon	Morris and Dishart[a]	Myers et al.[a]	Maynard and Sanders[a]
Paraffins			
Isobutane (iC_4)	0.7		
n-butane (nC_4)	4.8	7.0	4.3
Isopentane (iC_5)	8.5	9.3	10.2
n-pentane (nC_5)	3.4	4.5	5.8
Dimethyl butanes (C_6)	2.0	1.4	2.0
Methyl pentanes (C_6)	4.6	6.2	6.0
n-hexane	2.0	3.3	1.5
Dimethyl pentanes	2.4	1.4	1.9
Methyl hexanes	5.9	6.3	3.2
Trimethyl pentanes	11.1	8.5	9.4
n-heptane	1.2	2.0	2.0
Dimethyl hexanes	1.3	2.9	2.0
Methylethyl pentanes	1.4		0.4
Dimethyl hexanes	1.3		
Trimethyl hexanes	1.4		0.4
n-octane	1.3		
Naphthenes			
Methylcyclopentane	2.0	1.8	0.6
Cyclohexane	0.9		0.2
Methylcyclohexane	1.2	1.0	0.3
Other saturates	7.5		
Olefins			
Methylbutene	2.5	2.5	1.3
Pentene	0.8	0.8	1.6
Methylpentene	0.8	1.5	1.1
Other olefins	7.5	2.5	3.5
Aromatics			
Benzene	0.9	1.5	0.8
Toluene	6.5	5.9	12.2
Ethylbenzene	1.3	1.3	1.7
Xylenes	8.8	5.9	7.3
Propylbenzene	1.4		0.3
Methylethylbenzenes	2.8	1.5	1.6
Trimethylbenzene	7.1	1.7	2.3
Other aromatics	5.2		2.3
Total			
Saturates	62		62
Olefins	11		9
Aromatics	27		29

[a] Cited in Reference 139.

TABLE 6-23. AVERAGE GASOLINE VAPOR COMPOSITION[139]

Compound	Mean volume percent
Alkanes	
Propane	0.8
n-butane	38.1
Isobutane	5.2
Isopentane	22.9
n-Pentane	7.0
Cyclopentane	0.7
Dimethylbutane	0.7
Methylpentanes	3.6
n-Hexane	1.5
Methylcyclopentane	1.3
Dimethylpentanes	1.1
Trimethylpentanes	0.5
Alkenes	
Isobutylene	1.1
Methylbutenes	2.8
Aromatics	
Benzene	0.7
Toluene	1.8
Xylene	0.5

Evaporative emissions from automobiles, plus evaporative losses from gasoline marketing and storage, result in the presence of gasoline vapor components in all urban atmospheres. Evaporative emissions consist of the lighter components of gasoline, primarily C_4 and C_5 hydrocarbons. The exact composition of the emissions depends on the composition of the gasoline, on the temperature it reaches (in carburetor, fuel tank, storage tank; during delivery), and the degree of "weathering," that is, prior evaporation.[10] Analyses from several studies indicate that the light paraffins and light olefins constitute about 70 percent of carburetor emissions and about 90 percent of fuel-tank emissions. Isopentane and n-butane were by far the predominant hydrocarbons, making up about 50 percent of the total. Despite variations in gasoline composition, these two paraffins account for the major portion of all gasoline evaporation losses.[10]

Exhaust emissions from gasoline-fueled vehicles typically contain fuel components and low-molecular-weight hydrocarbons that are not present in the fuel. These low-molecular-weight hydrocarbons include methane, ethane, ethylene, acetylene, propylene, the C_4 olefins, and sometimes propadiene and methylacetylene. The fuel components include hydrocarbons with carbon numbers higher than butane (C_4).[10] The predominant hydrocarbons in auto exhaust, as reported in three separate studies, appear in Table 6-24.[10] As this table shows, the low-molecular-weight hydrocarbons--methane, ethylene, acetylene, and propylene--are high on each list. Toluene and isopentane seem to be the major fuel components.

Extensive studies have been conducted on the effect of gasoline composition on exhaust composition. Dishart and coworkers concluded that ethylene is formed from saturates and olefins--propylene and butene primarily from saturates,

TABLE 6-24. PREDOMINANT HYDROCARBONS IN EXHAUST EMISSIONS FROM GASOLINE-FUELED AUTOS[10]

Hydrocarbon	Fraction of total HC, vol % 62-Car survey[145]	 15-Fuel study[140]	 Engine-variable study[a,146]
Methane[b]	16.7	18	13.8
Ethylene[b]	14.5	17	19.0
Acetylene[b]	14.1	12	7.8
Propylene[b]	6.3	7	9.1
n-Butane	5.3	4	2.3
Isopentane	3.7	4	2.4
Toluene	3.1	5	7.9
Benzene[b]	2.4	--	--
n-Pentane	2.5	--	--
m- + p-Xylene	1.9	--	2.5
1-Butene[b]	1.8	3[c]	6.0[c]
Ethane[b]	1.8	--	2.3
2-Methylpentane	1.5	--	--
n-Hexane	1.2	--	--
Isooctane	1.0	--	--
All others	22.2	30	26.9

[a] Variables were air:fuel ratio and spark timing.
[b] Combustion products.
[c] Includes isobutylene.

and diolefins primarily from olefins--and that additional amounts of toluene, benzene, and xylenes are formed from higher aromatics and additional 2-methyl-2-butene from higher saturates.[140-142] Doelling et al.[143] concluded that gasoline composition had no effect on the total concentration of hydrocarbons in exhaust, but that the percentages of paraffins, olefins, and aromatics in exhaust were correlated with fuel composition. Neligan et al.[144] concluded that fuel olefinic exhaust emission is proportional to the olefin content of the fuel, but that the nature and concentration of the light, cracked products are independent of the olefin content of the fuel.

The use of catalytic converters has had a pronounced effect not only on the amount of hydrocarbons emitted from cars but also on the kinds. In general, oxidation catalysts have resulted in an increase in the percentage of paraffins, especially methane; and a decrease in percentage of olefins and acetylene. Typically, exhaust from a catalyst-equipped automobile contains about 62 percent paraffins, 17 percent aromatics, 18 percent olefins, and 3 percent acetylene; as compared with 40, 24, 26, and 11 percent, respectively, for automobiles without exhaust emission converters. The methane levels generally range from about 10 to 30 percent.[147,148] A study by Jackson produced the emission data for non-catalyst-equipped and catalyst-equipped cars presented in Table 6-25.[149] These data corroborate the decrease in olefins and acetylene cited above. The decrease in acetylene seen with the catalytic converter has implications for the use of acetylene as an indicator of auto exhaust emissions in source reconciliation studies (Section 6.3.1), since the mole percent of acetylene attributable to auto exhaust is declining. Furthermore, auto exhaust is not the only source of acetylene in urban atmospheres, as demonstrated by

TABLE 6-25. SUMMARY OF EXHAUST EMISSION DATA FOR NONCATALYST AND CATALYST-EQUIPPED GASOLINE-FUELED CARS BY MODEL YEAR[149]

	Noncatalyst-equipped				Catalyst-equipped		
	1970	1972	1973	1974	1975	1976	1977
No. of Calif. Cars	-	1	-	1	5	-	4
No. of Fed. Cars	1	-	3	8	9	2	-
Mileage	3,600	42,105	19,802	9,162	16,075	3,218	9,859
(km)	5,792	67,747	31,861	14,742	25,865	5,178	15,863
	Carbon, % of total hydrocarbon						
Nonreactive hydrocarbons							
Acetylene	7.4	10.7	7.8	7.7	2.5	3.6	0.3
Methane	6.2	6.3	4.9	4.7	11.3	9.8	28.0
Benzene	6.4	3.8	3.4	4.9	3.7	4.8	1.6
Ethane	1.2	0.9	1.0	1.0	2.6	3.0	4.5
Propane	0.1	0.0	0.1	0.1	0.3	0.3	0.3
Nonreactive total	21.4	21.7	17.1	18.4	20.4	21.6	34.7
Reactive hydrocarbons							
Ethylene	10.1	15.5	12.8	12.4	7.4	7.2	7.8
Toluene	11.7	11.4	9.1	7.5	6.5	7.2	7.7
Xylenes	9.7	2.3	4.1	7.7	5.9	7.3	2.0
Propylene	8.0	9.6	6.3	6.1	3.1	3.9	1.5
Trimethylpentanes	2.1	3.0	5.5	4.0	5.4	5.0	15.6
n-Butane	1.6	7.0	2.0	4.7	5.3	3.9	7.2
i-Pentane	4.4	5.2	4.5	3.6	5.4	4.5	5.9
Butenes	6.0	2.3	2.9	4.0	2.5	4.2	0.4
Methylpentanes	2.0	1.2	2.9	2.0	3.0	3.2	1.5
n-Pentane	0.6	2.1	1.4	1.3	2.1	2.1	0.3
Ethylbenzene	1.7	0.6	1.1	1.7	1.4	1.9	0.6
i-Butane	0.8	2.3	0.8	0.6	1.0	0.8	0.3
Other hydrocarbons	19.8	15.6	29.7	25.6	29.6	27.2	14.0
Reactive total	78.6	78.3	82.9	81.6	79.6	78.4	65.3
Hydrocarbon classes							
Paraffins	23.9	34.5	36.8	33.2	52.9	46.4	74.3
Olefins	32.0	31.1	25.7	25.8	16.4	17.0	9.9
Acetylene	7.4	10.7	7.8	7.7	2.5	3.6	0.3
Aromatics	36.7	23.7	29.7	33.3	28.2	33.0	15.6
	Hydrocarbon reactivity per gram						
Molar-based reactivity scales							
NO_2 formation rate	0.0542	0.0511	0.0467	0.0485	0.0366	0.0380	0.0222
Altshuller	0.0571	0.0556	0.0499	0.0518	0.0162	0.0892	0.0234
Methane exclusion	0.0167	0.0190	0.0166	0.0165	0.0132	0.0139	0.0109
Dimitriades	0.1612	0.1773	0.1548	0.1560	0.1210	0.1232	0.1078

TABLE 6-25 (continued).

	Noncatalyst-equipped				Catalyst-equipped		
	1970	1972	1973	1974	1975	1976	1977
No. of Calif. Cars	-	1	-	1	5	-	4
No. of Fed. Cars	1	-	3	8	9	2	-
Mileage	3,600	42,105	19,802	9,162	16,075	3,218	9,859
(km)	5,792	67,747	31,861	14,742	25,865	5,178	15,863
Carbon, % of total hydrocarbon							
Carbon-based reactivity scales							
Methane exclusion	0.9380	0.9370	0.9510	0.9530	0.8870	0.9020	0.7200
Cal. Air Res. Bd.	0.4808	0.4469	0.4160	0.4215	0.3300	0.3443	0.2456
Relative reactivity per gram (nonconverter car average = 100.0)							
Molar-based reactivity scales							
NO_2 formation rate	111.3	104.9	95.9	99.5	75.2	78.0	45.6
Altshuller	109.8	106.9	96.0	99.6	69.6	75.4	45.0
Methane exclusion	100.0	113.8	99.4	98.3	79.0	83.2	65.3
Dimitriades	101.3	112.5	98.2	99.0	76.8	78.2	58.4
Carbon-based reactivity scales							
Methane exclusion	98.7	98.6	100.1	100.3	93.4	94.3	75.8
Cal. Air Res. Bd.	112.8	104.8	97.6	98.9	77.4	30.7	57.6
Exhaust emissions, g/mi[a]							
Methane	0.21	0.06	0.20	0.09	0.08	0.09	0.08
Nonmethane HC	3.22	1.30	3.75	1.87	0.63	0.86	0.19
Total HC	3.43	1.36	3.95	1.96	0.71	0.95	0.27

[a] To convert g/mi to g/km, divide g/mi by 1.609.

Trijonis and Arledge, who found acetylene from major sources in Los Angeles in the following amounts: 2 mole percent from petroleum refinery operations; 5 mole percent from stationary source fuel combustion; 8 mole percent from waste burning and other fires; and 11 mole percent from gasoline-powered, light-duty vehicles.[150] To assume that auto exhaust is the only source of acetylene could mean the introduction of significant error depending on the quantity and profile of emissions being studied. For Los Angeles, the error introduced has been calculated to be less than 3 percent, however.[151]

The decrease in ethylene in exhaust emissions from catalyst-equipped vehicles is worthy of particular mention, because ethylene is known to be a phytotoxicant (Section 6.7). Data from the Jackson study[149] show that ethylene averaged 12.5 percent of the total hydrocarbons emitted from cars without oxidation catalysts (model year 1970 through 1974) and only 7.4 percent of total hydrocarbons emitted from catalyst-equipped cars (1975 through 1977 model years).

Jackson also evaluated the emissions in the same study by six scales used to indicate potential photochemical reactivity of hydrocarbons. All six showed that catalyst-equipped cars produced exhaust hydrocarbon mixtures that were less reactive than those from non-catalyst cars. The reductions in photochemical reactivity per gram ranged from about 10 to 35 percent. Thus, catalytic converters have not only reduced total hydrocarbon emissions but have also reduced the oxidant-forming potential of those emissions.[149]

Exhaust gases from gasoline-fueled autos contain organic compounds besides hydrocarbons, such as aldehydes, ketones, alcohols, ethers, esters, acids, and phenols. The concentration in exhaust of these oxygenates is about one-tenth that of the total hydrocarbon concentration. Aldehydes are generally believed to be the most important class of oxygenates. Formaldehyde is by far the predominant aldehyde, constituting about 60 to 70 percent of the total (by volume); acetaldehyde is next, at about 10 percent; and propionaldehyde, acrolein (acrylic aldehyde), benzaldehyde, and the tolualdehydes are all found in appreciable amounts. As might be expected, the compositon of the gasoline burned influences the composition of the aldehydes formed.[10]

Gasoline composition and catalytic converters are but two of many factors that influence the composition of exhaust gases from cars. Other factors include fuel composition, driving patterns, configuration of emission controls, ambient temperature and humidity, and individual automobile characteristics such as make, model year, age, engine size, air:fuel ratio, and spark timing. In addition, fuel additives can alter the exhaust hydrocarbon emissions. Of particular interest is the effect of lead additives. The use of tetraethyl lead (TEL) as a gasoline antiknock agent tends to increase exhaust hydrocarbon emissions directly and also indirectly, by promoting the buildup of engine deposits. According to one study, TEL directly increases hydrocarbon emissions by about 5 percent; the indirect effect, from accumulation of deposits, results in an additional 7 percent.[152] The composition of exhaust hydrocarbons is not affected by TEL.[153]

Just as the use of lead additives affects exhaust hydrocarbon emissions, so does their non-use; again, indirectly. To achieve the same octane and antiknock properties found in leaded gasoline, refineries must process more of the lower octane blending stocks such as light, straight-run gasoline; hydrocracked gasoline; and thermally cracked gasoline. These processes primarily involve conversion of naphthenes to aromatics and normal paraffins to isoparaffins.[139] In actual practice, gasolines of all grades generally have lower octane ratings now than in previous years. While aromatics in all gasolines, leaded as well as unleaded, have gradually increased over a period of years, the aromatic content of unleaded gasoline has not increased commensurately with the removal of lead; that is, the aromatic content is not high enough to attain the combined octane and antiknock properties of leaded gasoline.[154] Nevertheless, the increases in aromatic content that have occurred, along with possible future increases, are expected to affect the hydrocarbon composition of exhaust emissions. Benzene is considered the most toxic component of the aromatic fraction of gasoline vapor (Section 6.6). Toluene, xylenes, and other alkylated benzene derivatives are more toxic than benzene in acute exposures but less toxic in chronic exposures; they are also much less volatile than benzene.[139] On the other hand, benzene has low reactivity in atmospheric photochemical processes, whereas primary and secondary monoalkyl benzenes are highly reactive and tertiary monoalkyl benzenes and tolualdehyde are moderately reactive. Benzaldehyde, like benzene, is of low reactivity.[7,73]

An investigation by Nebel[155] of the benzene content of exhaust emissions from five catalyst-equipped cars (1975 Federal Test Procedure, model year 1975 cars) showed that benzene constituted an average of 2.86 percent of the total HC exhaust emissions over odometer readings of 80 to 32,180 kilometers (50 to 20,000 miles). Total HC exhaust emission increased with accumulated mileage from 0.25 g/km to about 0.56 g/km at 32,180 kilometers (0.4 g/mi to about 0.9 g/mi at 20,000 miles). Benzene exhaust emissions, as a percentage of total HC exhaust emissions, increased irregularly with the accumulation of mileage. Black et al.[138] have recently examined both exhaust and evaporative emissions for total hydrocarbons and for individual species of hydrocarbons, including benzene and toluene. Their results confirm other data in the literature which show that oxidation catalysts not only reduce the mass of exhaust hydrocarbons emitted but also remove a greater percentage of unsaturated olefinic, aromatic, and acetylenic emissions than of saturated paraffinic emissions. While evaporative control devices clearly reduced total hydrocarbon emissions, Black et al.[138] found that the effect of these devices on the composition of evaporative HC emissions was well-defined. Their study showed that both the benzene and total aromatic content of fuel influenced the benzene emission rate. Fuel benzene had a greater impact on evaporative emissions of benzene--since all evaporative benzene emissions come from the fuel--than on benzene in the exhaust, at least some of which is derived from the combustion process. In fact, dealkylation of higher aromatics appeared to be a significant source of exhaust benzene emissions when the vehicle was operated on a fuel-rich mixture. Data from the study showing differences in THC, benzene, and toluene emissions with differences in fuel composition and vapor pressure and emission control configuration are given in Table 6-26, derived from Black et al.[139] Increased gasoline aromaticity also affects exhaust emission rates for aromatic aldehydes from non-catalyst-controlled vehicles, as shown in Table 6-27.[156] Increased aromaticity likewise produces increased amounts of phenols in exhaust emissions in uncontrolled cars and, with as much as 46 percent aromatic fuels, in catalyst-equipped cars as well.[157] The effects of increased aromaticity on ambient air concentrations of aromatics appear to be negligible to date, as discussed in Section 6.4.

TABLE 6-26. EXHAUST, EVAPORATIVE, AND AGGREGATE EMISSIONS OF TOTAL HYDROCARBONS, BENZENE, AND TOLUENE FROM FOUR PASSENGER CARS (1963 THROUGH 1979 MODEL YEARS) AND FOUR FUELS[139]

			Fuel content		Exhaust emissions			Evaporative emissions[c]			Aggregate emissions		
Vehicle	Emission controls[a]	Fuel[b] (RVP)	Aromatics, %	Benzene, %	THC, g/mi	Benzene, % of THC	Toluene, % of THC	THC, g/mi	Benzene, % of THC	Toluene, % of THC	THC, g/mi	Benzene, % of THC	Toluene, % of THC
1963 Chevrolet	I	D (12.8)	25.9	1.8	4.03 ± 0.06	3.8	5.1	5.57 ± 1.18	0.6	1.7	9.60	1.9	3.1
		D-1 (12.8)	28.9	5.8	---	7.0	5.2	---	3.6	1.3	--	5.2	3.1
1977 Mustang-II	II	B (9.8)	43.4	1.5	2.78 ± 0.32	10.5	20.8	2.65 ± 0.23	1.8	8.3	5.43	6.2	14.7
		B-1 (9.8)	46.6	7.1	---	12.9	18.3	---	6.2	8.6	--	10.0	14.1
		C (12.3)	25.7	2.0	2.80 ± 0.13	6.8	6.0	3.61 ± 0.56	1.6	2.2	6.41	3.9	3.9
1978 Mercury Monarch	III	A (8.4)	27.4	0.3	1.03 ± 0.12	2.9	11.3	0.20 ± 0.04	0.5	7.0	1.23	2.5	10.6
		A-1 (8.4)	32.4	7.1	---	6.6	10.4	---	5.7	6.2	--	6.4	9.6
		B (9.8)	43.4	1.5	0.89 ± 0.12	3.4	17.7	0.47 ± 0.16	1.8	20.3	1.36	2.8	18.6
		C (12.3)	25.7	2.0	1.27 ± 0.18	2.6	4.1	0.75 ± 0.29	0.6	1.7	2.02	1.9	3.2
1979 Ford LTD-II	IV	B (9.8)	43.4	1.5	0.48 ± 0.14	5.1	15.9	0.31 ± 0.06	2.2	21.7	0.79	4.0	18.2
		B-1 (9.8)	46.6	7.1	---	7.0	13.9	---	7.1	22.8	--	7.0	17.2
		C (12.3)	25.7	2.0	0.51 ± 0.13	2.8	2.8	2.39 ± 0.32	0.5	1.0	2.90	0.9	1.3

[a] I = no evaporative controls, PCV; II = fuel tank canister, PCV, EGR, catalyst; III = single carburetor plus fuel tank canister, PCV, EGR, AIR, catalyst; IV = one canister each for fuel tank and carburetor, PCV, EGR, AIR, and catalyst (see Table 6-21 for control device descriptions).

[b] A = regular, unleaded summer blend; A-1 = A with added benzene; B = premium, unleaded summer blend; B-1 = B with added benzene; C = regular, unleaded winter blend; D = regular, leaded summer blend; D-1 = D with added benzene. RVP = Reid Vapor Pressure, given in parentheses.

[c] Composite evaporative emissions using SHED procedure ("Sealed Housing for Evaporative Determination").

[d] To convert g/mi to g/km divide g/mi by 1.609.

TABLE 6-27. INCREASE IN EXHAUST EMISSION RATES OF AROMATIC ALDEHYDES FOR NON-CATALYST GASOLINE CARS WITH INCREASE IN FUEL AROMATICITY[156]

Fuel	Aromatics, mole %	Total aldehydes, ppm	Aromatic aldehydes, ppm
Unleaded premium	46.6	65	13.6
Leaded premium	30.8	72	6.1
Leaded regular	27.3	69	5.8

Precipitated by the energy crisis, an additional development that will affect the concentration and composition of hydrocarbon emissions from mobile sources is the possible use of alternative liquid fuels such as gasoline-alcohol or gasoline-ether mixtures. Comparison of vehicle emissions data from different studies is difficult because of the variety of test conditions, measurement techniques, fuels, engine and other modifications, and emission control system configurations used in the respective studies. Nevertheless, certain qualitative trends in emissions from alternate fuels are by now discernible from data in the literature.

Work reported in 1975 by Brinkman et al.[158] indicated that adding methanol to gasoline--without carburetor modifications--decreased CO emissions; decreased volume-based fuel economy; decreased driveability and performance; and did or did not affect the mass of HC and NO_x emissions, depending on the air-fuel ratio, car-fuel combinations, and other factors. They found also that the research octane number (RON) increased almost linearly with the addition of methanol but that the motor octane number (MON) did not. They further found that RON and MON of methanol-gasoline blends (hereafter referred to as "methagas") are not predictive of the road octane number of the blends. A study by Bernhardt and Lee[159] showed that organic emissions from a 100 percent methanol-fueled car contain only a small percentage of hydrocarbons, mainly methane, ethane, and ethylene. Emissions of methanol and total aldehydes, however, using the same engine with the same compression ratio, are significantly higher with methanol than with gasoline. Total aldehydes in the exhaust are about twice as high with methanol as with gasoline. The total aldehydes can be reduced substantially, however, by increasing the compression ratio or by adding water to the pure ethanol. The overall emission rates for hydrocarbons, as determined by hot FID corrected by a factor obtained from GC analysis, were as shown in Table 6-28.[159] (Using the Federal emission test cycle, the vehicle tested emitted 2.79 g/km (4.5 g/mi) from gasoline and 1.55 g/km (2.5 g/mi) from pure methanol. The vehicle would not have met the 1975 Federal emission standard for HC of 0.93 g/km (1.5 g/mi).[159]

TABLE 6-28. TOTAL HYDROCARBON EMISSION RATES (ECE TEST CYCLE) FOR CAR FUELED WITH GASOLINE, METHANOL, OR A 15% METHANOL-85% GASOLINE MIXTURE[159]

Fuel	Test	HC emissions, g/test	HC emission, % of HC emissions from gasoline
Gasoline	Cold start	9.8	100
	Hot start	7.9	100
Methanol	Cold start	12.0	122
	Hot start	5.7	72
15% methanol-85% gasoline	Cold start	8.3	85
	Hot start	6.5	82

Asked to grant a waiver permitting the use of 10 percent ethanol in gasoline, EPA[160] in 1978 studied exhaust and evaporative emissions from 11 passenger cars tested by the Federal Test Procedure (FTP). Two gasoline and three gasohol (ethanol-gasoline) fuels were used in four cars equipped with three-way conversion (TWC) catalysts and in seven equipped with oxidation catalysts. Evaporative emissions were determined by the SHED procedure ("Sealed Housing for Evaporative Determination") and were also measured by gas chromatography. The researchers concluded from their data that combustion of a 10 percent ethanol-90 percent gasoline mixture: (1) increased evaporative HC emissions by about 50 percent; (2) decreased exhaust HC emissions by about 9 percent; (3) increased aggregate HC emissions (exhaust plus evaporative); (4) decreased fuel economy (carbon balance method) by about 2 percent; (5) increased NO_x emissions by about 7 percent; and (6) decreased CO emissions by about 35 percent.

Three-way conversion catalyst systems (TWC), as employed in the EPA tests cited above, provide for control of HC, CO, and NO_x and generally require the use of a closed-loop feedback control system for the air/fuel metering system in order to maintain a stoichiometric air/fuel ratio. When a fuel such as ethanol is added to gasoline, the stoichiometric air/fuel ratio is changed. Conventional air/fuel metering systems do not compensate for this change. A further study of HC emissions (FTP) from a TWC-equipped car (Volvo) fueled by ethanol-gasoline or methanol-gasoline blends resulted in the exhaust emissions shown in Table 6-29.[161]

Lang and Black,[162] in a recent EPA study, found similar results in tests of two catalyst-equipped passenger cars fueled with five different fuel blends. The FTP cycles and SHED procedures were used to determine exhaust

TABLE 6-29. EXHAUST EMISSIONS FROM VEHICLE EQUIPPED WITH THREE-WAY CONVERSION CATALYST AND FUELED WITH GASOLINE, ETHANOL-GASOLINE, OR METHANOL-GASOLINE[161]

Fuel[a]	Exhaust emissions, g/mi[b]		
	HC	CO	NO_x
No catalyst, 100% gasoline	0.93	13.68	2.47
TWC			
100% gasoline	0.14	3.19	0.11
10% EtOH-905 gas	0.31	3.90	0.11
20% EtOH-80% gas	0.24	2.77	0.14
30% EtOH-70% gas	0.11	2.61	0.07
40% EtOH-60% gas	0.14	0.78	1.77
50% EtOH-50% gas	0.22	0.90	1.55
10% MeOH-90% gas	0.16	3.20	0.09
20% MeOH-80% gas	0.15	3.20	0.05

[a] EtOH = ethanol; gas = gasoline; MeOH = methanol.

[b] To convert g/mi to g/km, divide g/mi by 1.609.

(tailpipe) and evaporative HC emissions. In addition, tailpipe and evaporative emissions were collected in Tedlar bags and analyzed for THC and ethanol by gas chromatography. The two cars tested, a 1977 Ford Mustang II and a 1979 Ford LTD II, differed somewhat in their emission control configurations. Both were equipped with EGR, catalyst, and PCV. The LTD had an AIR injection system and two carbon canisters for vapor control, one each for the fuel tank and carburetor. The Mustang had one canister for fuel tank vapor control. In these tests, the addition of ethanol to the base fuel produced for both cars: (1) a decrease in exhaust THC emissions; (2) a decrease in CO emissions; (3) an increase in NO_x emissions; and (4) a substantial increase in evaporative emissions. Little change in fuel economy was observed with either vehicle. Lang and Black noted that increases in fuel vapor pressure when ethanol is added contributes to differences in evaporative emissions, but that those changes do not account for all the increase observed. One gasohol (fuel 5) was blended to match the vapor pressure of the base fuel (fuel 3) and increases in evaporative emissions were still observed. They concluded that the vapor control canisters may selectively adsorb and retain ethanol because it is a more polar compound than the components of gasoline; and that the purge period between tests was thus too short for effective removal of ethanol vapor and regeneration of canister storage capacity. The work of Furey and King[163] had indicated the same selective adsorption of polar compounds. The effects of fuel composition on the emissions of THC and ethanol emission rates from the two test vehicles are shown in Figure 6-3.[162] Basic specifications for the five test fuels are given in Table 6-30.

TABLE 6-30. TEST FUEL SPECIFICATIONS[162]

Properties	Fuel 1	2	3	4	5
Vapor pressure (RVP)	9.15	9.10	9.85	9.65	9.40
IBP, °F	91	101	89	95	94
Ethanol (% vol)	1.4	6.2	0.86	8.1	10.1
API gravity	59.8	58.7	57.5	56.5	52.6
% Paraffin[a]	69.7	67.5	52.1	46.4	37.7
% Olefin[a]	0.4	0.6	17.2	16.6	17.6
% Aromatic[a]	28.5	25.7	29.8	28.9	34.6

[a] Determined by fluorescence indicator analysis (FIA).

Although methanol and ethanol have been suggested as technologically suitable fuel extenders, methyl tertiary butyl ether (MTBE) has also been shown to be a suitable blending component for gasoline. The use of MTBE as an extender provides a means for using methanol--since MTBE is synthesized from methanol plus isobutylene--without incurring some of the disadvangates associated with adding methanol directly to gasoline.

Hydrocarbon emissions from one prototype and one production car fueled with gasoline, gasohol, gasohol purged with nitrogen to reduce volatility ("adjusted gasohol"), or gasoline containing MTBE were determined by Furey and King.[163] Their test results showed that evaporative emissions were increased significantly by the addition of 10 percent ethanol to gasoline but were increased less by the additon of 15 percent MTBE to gasoline. Total evaporative emissions from the production car, not equipped with a closed-loop carburetor system, were higher with gasohol, adjusted gasohol, and MTBE than with gasoline.

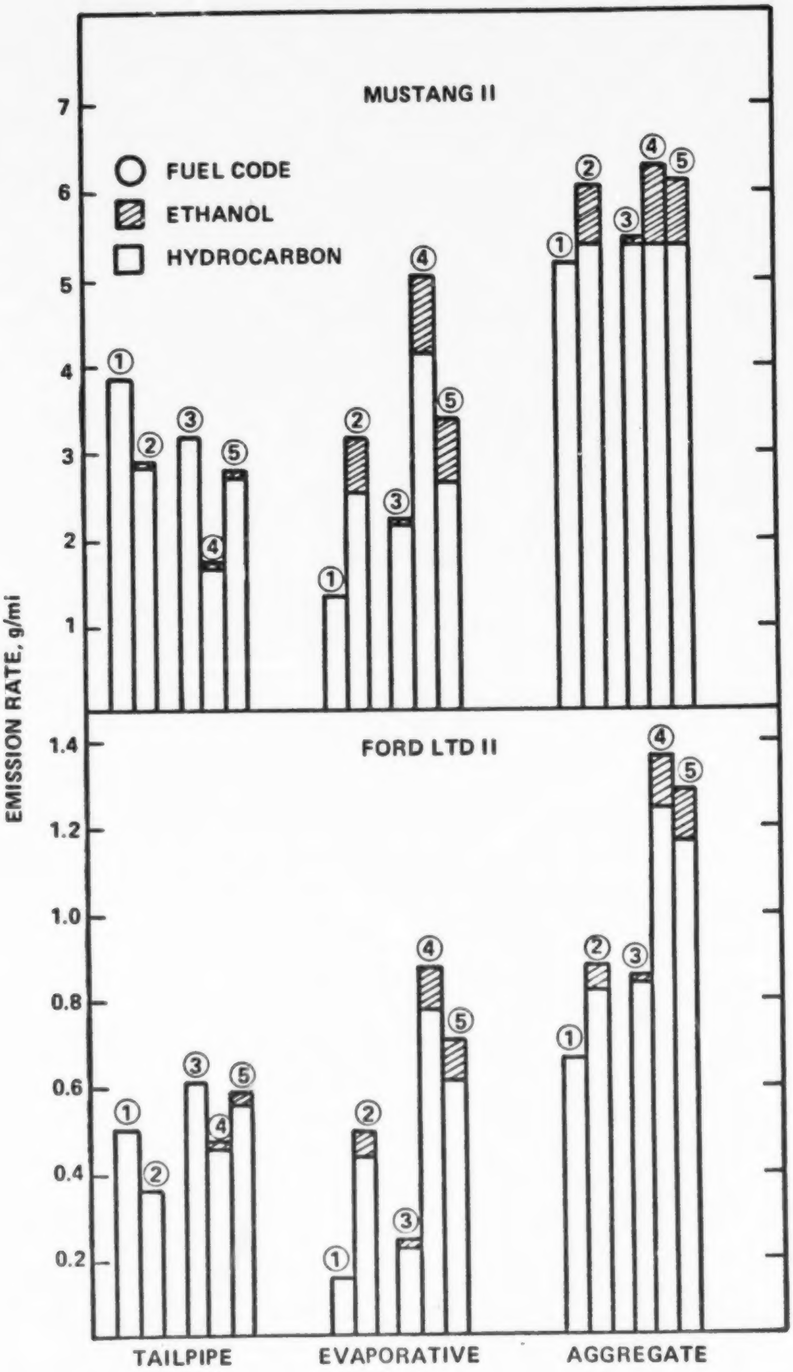

Figure 6-3. Effects of fuel composition on THC and ethanol emission rates.[162]

Total evaporative emissions from the prototype car, which was equipped with a closed-loop system, were higher with the two gasohols than with gasoline, but were essentially unchanged with the 15 percent MTBE-85 percent gasoline blend. Exhaust emissions of HC, CO, and NO_x from the production car were lower with gasohol and MTBE than with gasoline, but differences in these exhaust emissions from respective fuels in the prototype car were small. Furey and King also determined, by comparing "inlet vapor" going to the canister with "break-through" vapor from the canister, that ethanol and MTBE, both of which are polar compounds, are selectively adsorbed in the canister. It should be noted that ethanol has been reported to be moderately reactive photochemically but that MTBE is expected to have low reactivity. The potential for photochemical reactivity of evaporative emissions from gasohol-fueled or MTBE-gasoline fueled vehicles will depend in part, then, on whether such emissions are from canister inlet lines from the fuel tank and carburetor or whether they are vapors that have already passed through the canister(s).

Naman and Allsup[164] determined exhaust and evaporative HC emissions and fuel economy on eight test vehicles fueled by gasoline (Indolene), by gasohol (10 percent ethanol-90 percent gasoline), "methagas" (10 percent methanol-90 percent gasoline), 7 percent MTBE in gasoline, and 7 percent tert-butyl alcohol (TBA) in gasoline. Overall, decreases in fuel economy were seen with all the blends compared to gasoline. The decreases were greatest with methagas and least with MTBE. Emissions tests from the blends as compared with gasoline showed that (1) exhaust HC emissions were reduced 5 to 32 percent; (2) exhaust NO_x emissions ranged from unchanged to slightly increased, depending on the fuel and emission controls; (3) exhaust CO emissions were reduced 8 to 46 percent; and (4) evaporative emissions increased, ranging from 5 percent with TBA to 93 percent with methagas. Tests by Harrington et al.[165] showed clear directional changes in exhaust emissions from vehicles fueled by 20 percent MTBE-80 percent gasoline. With the MTBE blend, HC emissions decreased 20 to 30 percent, CO emissions decreased 40 to 50 percent, and NO_x emissions increased 12 to 22 percent. Fuel economy was not compromised by the addition of MTBE, apparently because the reduction in heating value of the fuel was offset by improved efficiency at the leaner air/fuel ratio produced by the introduction of MTBE.

Several studies have been conducted on the presence and levels of "unregulated pollutants," i.e., non-criteria pollutants in exhaust from vehicles fueled with gasohol, methagas, or MTBE blends. In the study cited earlier, Naman and Allsup[164] measured aldehydes in exhaust from vehicles equipped with oxidation catalysts or TWC catalysts and fueled with 10 percent ethanol, 10 percent methanol, 7 percent MTBE, or 7 percent TBA in gasoline. Exhaust emissions of aldehydes in cars with oxidation catalysts were unchanged with gasohol, were 50 percent higher with methagas, 22 percent lower with MTBE, and 6 percent lower with TBA relative to gasoline. Aldehydes in exhaust from cars equipped with TWC catalysts were two times higher with gasohol, unchanged with methagas, 1.8 times higher with MTBE, and 2.3 times higher with TBA relative to gasoline. Aldehydes were measured in this study by FID, concentrations being corrected according to the FID response to standards of these oxygenates.

Harrenstien[166] used a combined 2,4-dinitrophenylhydrazone gas chromatographic method specific for C_1 through C_5 aldehydes to measure them in exhaust from cars fueled with gasohol or methagas blends. Results of the study showed the following:

1. Total aldehydes in exhaust increased, relative to gasoline, 25 percent in 20 percent ethanol, 10 percent in 20 percent methanol, and 30 percent in 30 percent methanol.
2. Aldehyde concentrations in exhaust are more a function of fuel blend than equivalence ratio (air/fuel ratio relative to the stoichiometric ratio).
3. Total aldehyde concentrations for the alcohol blends tested ranged from 80 to 110 ppm (compound). Composition of the total was 70 to 90 percent formaldehyde, 5 to 22 percent acetaldehyde, 1 to 4 percent acetone (a secondary aldehyde, or ketone), 1 percent propionaldehyde, and 3 to 6 percent acrolein (acrylic aldehyde).

Data from a study by Matsuno et al.[167] indicate that in exhaust from methagas-fueled vehicles, hydrogen cyanide, NO_x, NH_3, THC, and photochemical reactivity decrease as the proportion of alcohol increases. Their data showed that formaldehyde and unburned methanol can be eliminated by the use of catalysts. Using ethanol-gasoline blends, they showed that ethylene in exhaust increases with an increase in ethanol, whereas hydrocarbons $>C_5$ decrease as ethanol increases. Again, catalysts reduce the amount of ethylene produced. When neat ethanol was used, HC were barely detectable in the exhaust; 86 percent of the carbon detected was attributable to unburned ethanol. The total aldehyde content of exhaust was shown to increase with increases in the alcohol content, methanol or ethanol, except for acrolein, which decreased as the alcohol content increased. Aromatics and their aldehydes (e.g., benzaldehyde and tolualdehyde) decreased with increasing alcohol content. Formic acid in the exhaust increased rapidly with increases in methanol, but acetic acid decreased slightly. With ethanol, the reverse was true.[167]

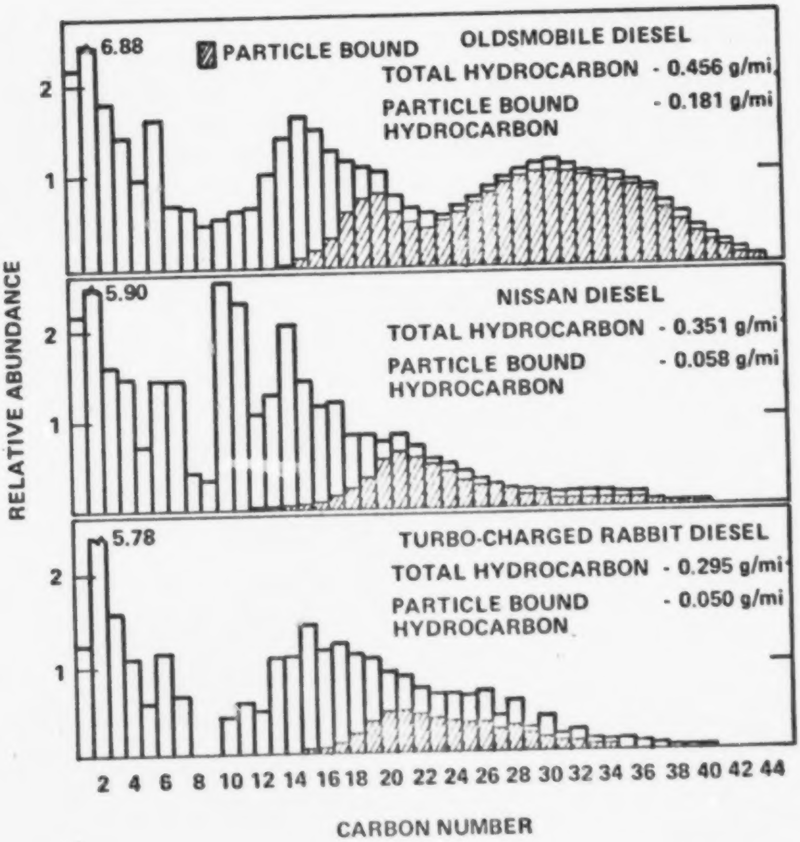

Figure 6-4. Distribution of diesel hydrocarbon exhaust emissions, by carbon number, between gas-phase and particulate forms.[170]

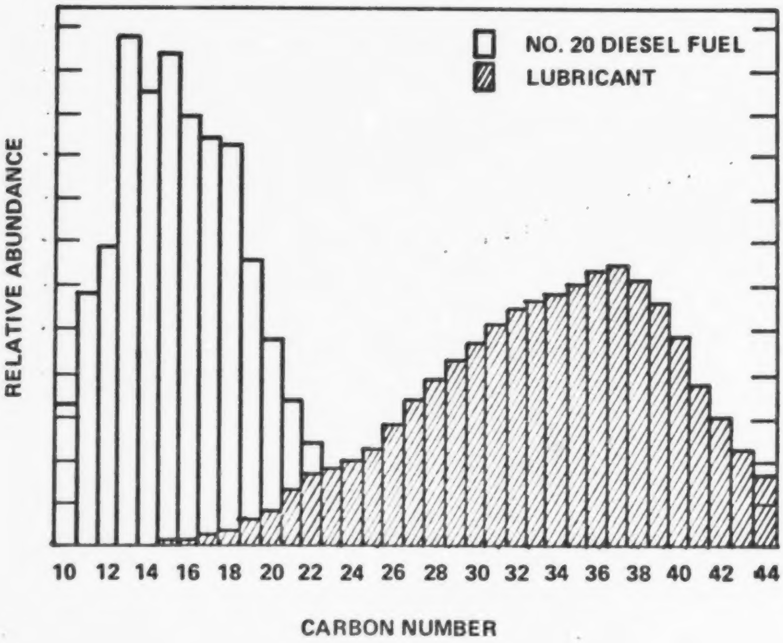

Figure 6-5. The distribution of hydrocarbons in diesel fuel and lubricant according to carbon number.[170]

TABLE 6-31. EMISSION RATES FOR HYDROCARBONS IN EXHAUST FROM TWO DIESEL VEHICLES[171]

(g/mi)[a]

Compound	1975 Peugeot	1973 Nissan
Methane	0.0121	0.0135
Ethane	0.0021	0.0009
Propane	0.0010	~0
Acetylene	0.0120	0.0129
Benzene	0.0092	0.0073
Ethylene	0.0413	0.0280
Propylene	0.0137	0.0094
Total nonreactive HC	0.0364	0.0346
Nonreactive HC, % of total HC	12.0	14.0
Methane, % of total HC	4.0	5.5
Total HC (hot FID analysis)	0.304	0.247

[a] To convert g/mi to g/km, divide g/mi by 1.609.

Diesel emissions are almost exclusively exhaust emissions. The gas-phase hydrocarbon fraction of diesel exhaust is complex and shows a bimodal distribution by carbon number. The fraction consists of light, cracked hydrocarbons and of heavy fuel-like components ranging up to as high as C_{40}.[134,168-170] Except for methane, the light, cracked hydrocarbons are mainly olefins. Ethylene, acetylene, and propylene are the predominant light hydrocarbons, with smaller amounts of C_4 olefins and even smaller amounts of C_5 and C_6 olefins.[134] Researchers at EPA[170] have found that the C_{10}-C_{40} organics are dominated by unburned fuel and lubricant components. Some of the organics in this range are particle-bound and some are gas-phase. The distribution of diesel exhaust hydrocarbons according to carbon number is shown in Figure 6-4. The exhaust hydrocarbons in the C_1 to C_{10} range result from the combustion process, cracking from higher-molecular-weight organics. Those emitted in the C_{10} to C_{40} range result mainly from unburned fuel in the C_{10} to C_{25} range and from lubricant in the C_{15} to C_{40} range. Partial combustion and rearrangement compounds occur in this range also.[170] For comparison, the distribution of hydrocarbons, by carbon number, in diesel fuel and lubricant is shown in Figure 6-5.[170] The No.2D diesel fuel used was composed of 66.2 percent paraffins, 1.3 percent olefins, and 32.5 percent aromatics, as determined by FIA.[170] Emission rates for low-molecular-weight hydrocarbons in exhaust of two diesel vehicles, obtained with the 1975 Federal Test Procedure (FTP), are shown in Table 6-31.[171]

It should be pointed out here that the "hot FID" procedure used to collect these and similar data uses a hot filter in the sampling probe in order to preserve in the vapor phase those hydrocarbons emitted. At ambient air temperatures, higher-molecular-weight hydrocarbons may react chemically, condense and be adsorbed or migrate to already formed particulate matter, or possibly even evaporate or desorb from particles.[7,172,173] Though some ambient air data have been reported[174] in which hydrocarbons $>C_{12}$ were present in the vapor phase, complications with adsorption and desorption of these compounds during collection, coupled with the fact that gas chromatographic columns often produce breakdown products in that carbon number range, detract from the acceptability of such data. Some of the compounds $>C_{12}$ should, according to their individual vapor pressures, occur in the vapor phase. However, hydrocarbons emitted from automobiles are not emitted as pure compounds in isolation from other compounds and from particles. Consequently, the vapor pressures of the individual compounds cannot be used to determine the phase in which compounds $\gtrsim C_{12}$ are likely to be found at ambient air temperatures. Furthermore, once hydrocarbons are absorbed by or adsorbed onto particles, the Kelvin effect influences the vapor pressures of the materials in the particulate matter.[7,173]

Particulate emissions from mobile sources--including their formation, their role in photochemical processes, and their health effects--are treated in two recent EPA publications.[61,175]

Low-molecular-weight aldehydes have also been found in diesel exhaust by many workers. Formaldehyde has been reported most often, followed by acrolein.[10] Vogh[176] measured the following aldehydes in one diesel exhaust sample: formaldehyde (18.3 ppm); acetaldehyde (3.2 ppm); acrolein, acetone, propionaldehyde, and isobutyraldehyde (2.9 ppm); _n_-butyraldehyde (0.3 ppm); crotonaldehyde and valeraldehyde (0.4 ppm); hexanaldehyde (0.2 ppm); and benzaldehyde (0.2 ppm). Data obtained by Braddock and Gabele[171] showed the dependence of diesel aldehyde emissions on fuel. These data are presented in Table 6-32.[171]

TABLE 6-32. ALDEHYDE EMISSIONS FROM DIESEL VEHICLES OPERATING ON FIVE DIFFERENT FUELS, 1975 FTP[171] (mg/mi)[a]

Compound	Test fuel and number (n) of tests				
	Jet A (n=7)	Local no. 1 (n=7)	Nat'l avg. no. 2 (n=4)	No. 2-D n=7	Nissan no.2 n=5
Formaldehyde	21.9	16.9	48.2	40.8	25.4
Acetaldehyde	7.5	7.4	11.9	8.2	10.8
Propionaldehyde + acrolein	5.4	6.2	8.7	5.5	4.7
Crotonaldehyde	0.5	~0	0.6	~0	6.4
Hexanaldehyde	0.3	0.5	0.4	0.1	~0
Benzaldehyde	0.9	7.8	0.8	1.4	0.3
Total aldehydes	36.3	38.9	60.1	55.9	47.6
Total HC (hot FID) % Aldehydes	344 10.6%	304 12.8%	471 12.8%	489 11.4%	334 14.2%

[a] To convert mg/mi to mg/km, divide mg/mi by 1.609.

In a study of catalyst-controlled diesel engines, Marshall et al.[177] found that all four of the noble metal catalytic converters tested effected 10 to 50 percent reductions in peak emission rates of hydrocarbons. Detailed examination by gas-liquid chromatography indicated that the catalysts tended to oxidize preferentially the unsaturated hydrocarbons. The remaining high-molecular-weight hydrocarbons were, as a result, predominately the saturated compounds. Because peak emission rates of aldehydes occurred at light load (low exhaust temperature), the catalysts had little influence on peak emission rates. Average emission rates, however, were reduced substantially.

Since diesels emit hydrocarbons almost exclusively from the tailpipe, and gasoline-powered cars emit from both tailpipe and evaporative sources, diesels generally emit fewer net gas-phase hydrocarbons. Diesel exhaust from uncontrolled vehicles can, however, contain higher concentrations of gas-phase hydrocarbons than the exhaust of catalyst-equipped gasoline-fueled vehicles.[178] While the net production of exhaust HC emissions is important from the health standpoint, the contribution of the kind of hydrocarbons emitted from diesels to the formation of photochemical smog products is also important. Spicer and Levy[179] critically reviewed the nature and photochemical smog reactivity of diesel engine exhaust organic components. Although an enumeration of the assumptions made and a description of the reactivity scales employed are beyond the scope of this paper, a summary of their findings on the reactivity of the two exhaust organic fractions is presented in Table 6-33.[179] Though a direct comparison of gasoline and diesel exhaust emissions is difficult because different test cycles are used, these data and those of Landen and Perez[180] indicate that the calculated reactivity of diesel exhaust, on a ppm emission basis, is fairly low relative to gasoline exhaust.

Because transportation sources in general, and highway vehicles in particular, are major contributors to hydrocarbons in ambient air, emissions from these sources strongly influence the composition of hydrocarbon mixtures in urban atmospheres. Table 6-34 summarizes emission characteristics of autos fueled by gasoline, alcohol-gasoline blends, ether-gasoline blends, and diesel fuels, since changes in patterns of fuel use or in the percentage of diesel- versus gasoline-fueled vehicles in operation will result in qualitative as well as quantitative changes in hydrocarbons emitted from mobile sources.

TABLE 6-33. SUMMARY OF REACTIVITY OF DIESEL EXHAUST HYDROCARBON EMISSIONS AND PERCENTAGE CONTRIBUTIONS OF LOWER-MOLECULAR-WEIGHT HYDROCARBONS AND ALDEHYDES[179]

Gas-phase	Concentration		Reactivity index units			
HC fraction	ppm	%	NO_2[a]	O_3[a]	E.I.[a]	Aerosol[a]
C_1-C_5	38.7	38	90.1	223.4	38.1	36.6
C_1-C_{22}	70.0	69	180.3	483.0	98.0	314.0
Aldehydes	32.2	31	193.2	460.4	119.3	32.2
Total HC	102.2	100	373.5	943.4	217.3	346.2
	Percentage contribution					
C_1-C_5, % of total	55		50	46	39	12
Aldehydes, % of total	46		108	95	122	10

[a] NO_2 photooxidation reactivity; ozone-forming potential; potential for forming components causing eye irritation; and aerosol-forming potential.

TABLE 6-34. SUMMARY OF EMISSION CHARACTERISTICS FOR AUTOS FUELED BY GASOLINE DIESEL, AND ALCOHOL-GASOLINE OR ETHER-GASOLINE BLENDS

Auto, control device, or fuel	Emission characteristics
Gasoline-fueled, uncontrolled	1. Exhaust emissions about 40% paraffins; 24% aromatics; 26% olefins; 11% acetylene. 2. Main components of exhaust emissions: methane, ethane, acetylene, ethylene, propylene, C_4 olefins, toluene, benzene, *n*-butane, *n*-pentane, isopentane, xylene; aldehydes and some organic acids, ketones, phenols. 3. Evaporative emissions: 70% of carburetor emissions are light paraffins and olefins; 90% of fuel-tank emissions are light paraffins and olefins.
Gasoline-fueled, catalytic converters	1. Exhaust emissions: about 62% paraffins, 17% aromatics, 18% olefins; 3% acetylene. Methane is about 10-30% of exhaust emissions. 2. Catalysts preferentially oxidize unsaturated HC. 3. Lower reactivity per gram HC emissions than from uncontrolled gasoline-fueled. 4. Lower net HC emissions than from uncontrolled gasoline-fueled.
Lead additives in gasoline	1. Presence of TEL increased HC emissions. 2. Absence of TEL (or TML) necessitates higher aromaticity of gasoline to achieve higher octane ratings.
Ethanol-gasoline blends (relative to gasoline)	1. Decreased exhaust THC emissions. 2. Increased evaporative THC emissions. 3. Increased aggregate (exhaust plus evaporative) THC emissions. 4. Aldehydes in exhaust increased from non-catalyst cars; unchanged from cars with oxidation catalysts; increased from cars with TWC catalysts. 5. Increased in ethylene from non-catalyst cars; no increase from cars with oxidation catalysts. 6. Increases in acetic acid with increasing alcohol content.
MTBE-gasoline blends (relative to gasoline)	1. Decreased exhaust THC emissions. 2. Increased evaporative THC emissions, but less than with alcohol-gasoline blends. 3. Aldehydes increased from cars with TWC catalysts; decreased from cars with oxidation catalysts.

TABLE 6-34 (continued).

Auto, control device, or fuel	Emission characteristics
Methanol-gasoline blends (relative to gasoline)	1. Emission rate of exhaust THC not appreciably changed; composition changed. 2. Higher methanol in exhaust. 3. Aldehydes in exhaust increased from non-catalyst cars; no significant change in aldehydes with TWC catalysts; higher aldehydes with oxidation catalysts. 4. Decreases in exhaust NH_3, HCN, photochemical reactivity with increases in % alcohol. 5. Increases in exhaust formic acid with increases in % alcohol.
100% Methanol	1. Higher cold-start HC emissions than from gasoline-fueled. 2. Significantly lower hot-start HC emissions than from gasoline-fueled. 3. Exhaust emissions: mainly methane, ethane, ethylene. 4. Significantly higher methanol and aldehyde emission than gasoline-fueled (aldehydes reduced by increasing compression ratio or adding water to methanol).
Diesels	1. Almost exclusively exhaust emissions. 2. Emissions: light, cracked HC, mainly methane, ethylene, acetylene, propylene; also aldehydes (C_1-C_6), including acrolein), and acetone. 3. Lower reactivity per gram HC emissions than from gasoline-fueled. 4. Lower net HC emissions than from gasoline-fueled. 5. Higher carbonyl emissions (aldehydes, ketones).

6.4 AMBIENT AIR CONCENTRATIONS

Ambient air monitoring for hydrocarbons is not required under EPA regulations for purposes of enforcing the HC NAAQS.[5] The monitoring of hydrocarbons that is conducted by the states is for the purpose of controlling oxidant levels. Thus, states have measured ambient air levels of HC primarily to obtain data that can be used as input to the respective models used to determine the percentage reductions in HC emissions that are needed to attain and maintain the NAAQS for ozone. Hydrocarbons in ambient air are also measured by the states and by EPA for other purposes, including: (1) to verify models; (2) to determine the effectiveness of control strategies; (3) to study oxidant transport phenomena; and (4) to obtain empirical data to verify reaction mechanisms and kinetics.

Since routine monitoring has not been required, most of the data available have been obtained from field studies conducted by EPA, alone or in conjunction with state and local control agencies or contractors. Most of the data presented in this section were obtained by the Environmental Sciences Research Laboratory (ESRL), ORD, EPA, Research Triangle Park; or by its contractors and grantees. In many instances these data have not yet been published. In other instances, data from the open literature are available and have been presented. Some of the data given here are 24-hour averages of total NMHC, calculated from 2-hour or 3-hour averages obtained during diurnal studies. Some are "instantaneous" concentrations measured in grab samples that are taken over a period of 5 to 10 minutes. Some of the data describe concentrations of individual hydrocarbons, some classes of hydrocarbons, and some total nonmethane hydrocarbons. These data are presented in these various forms partly because they are available only in these forms and partly in order (1) to compare them with data that appeared in the 1970 criteria document; (2) to compare ranges in ambient air levels with levels used in clinical and toxicological studies and with levels found in occupational exposures; (3) to compare profiles--qualitative and quantitative--of hydrocarbon mixtures in ambient air from one city to another; and (4) to compare profiles of ambient air hydrocarbon mixtures with auto exhaust and with gasoline vapor.

One quite important point must be noted at this juncture since it relates to comparisons between ambient air HC concentrations and exposure levels reported in occupational, clinical, or toxicologic studies. Most of the ambient air data reported in this section have been calculated in terms of ppm or ppb carbon (C), largely because the calibration gas used for most FID measurements is methane, CH_4, which contains one carbon atom per molecule; and because mixtures cannot be expressed in terms of compound concentration. Data reported by physicians and toxicologists are generally expressed as ppm or ppb compound. Atmospheric concentrations are expressed as ppm C or ppb C by multiplying the concentration of the compound by the number of carbon atoms in the compound. An example at this point may serve to clarify the difference. Pentane contains five carbons. A concentration of 20 ppb compound of pentane is equivalent to a concentration of 100 ppb C, since the compound concentration is multiplied by the number of carbons in the compound.

In a recently published compendium, Graedel[36] has documented the detection in ambient air of more than 1000 organic compounds. Five sources account for the bulk (in terms of number of entries) of the detected, identified substances: gasoline-powered vehicles, diesel vehicles, tobacco smoke, turbines, and vegetation. Ambient air concentrations for gas-phase hydrocarbons as reported in Graedel's monograph are summarized in Table 6-35.[36] These data do not include

TABLE 6-35. AMBIENT AIR CONCENTRATIONS OF HYDROCARBONS REPORTED BY GRAEDEL[a]

Compound	Concentration range, ppb (unless specified)
ALKANES	
Methane	1.3-4.0 ppm
Ethane	0.05-95
Propane	12-94
Butane	0.01-182
Isobutane	0.06-35
2,3-Dimethylbutane	3.8
Pentane	0.023-64
Isopentane	0.1-101
2-Methylpentane	5-12
3-Methylpentane	3-11
2,2-Dimethylpentane	1-2
2,3-Dimethylpentane	2
2,4-Dimethylpentane	0.3-13
2,2,4-Trimethylpentane	17
Hexane	4-27
2-Methylhexane	10-28
3-Methylhexane	10
Heptane	0.2-34
2-Methylheptane	3.4
Octane	0.04-3.4
Nonane	0.1-9.0
Decane	1.0-11.2
Undecane	0.95-8.8
Dodecane	1.3-5.1
Hexadecane	0.16-1.0
ALKENES AND ALKYNES	
Acetylene	0.2-227
Ethene	0.7-700
Propene	1-52
Propadiene	2-4
Propyne	1-6
1-Butene	1-6
2-Methyl-1-butene	1-19
Isobutene	1-6
1,3-Butadiene	1-9
Isoprene[b]	0.2-2.9
cis-2-Butene	1-11
trans-2-Butene	1-3

TABLE 6-35 (continued)

Compound	Concentration range, ppb (unless specified)
2-Methyl-2-butene	2-18
1-Pentene	1-12
4-Methyl-1-pentene	1-3
cis-2-Pentene	2-6
trans-2-Pentene	2-4
2,4-Dimethyl-2-pentene	3-10
1-Hexene	3
cis-2-Hexene	4-8
TERPENES[b]	
α-Pinene	0.93-1.20
β-Pinene	0.14-0.40
Myrcene	0.74-1.0
Limonene	0.06-5.7
ALICYCLICS	
Cyclopentane	2-14
Cyclopentene	2-6
Cyclohexane	3-6
Methylcyclohexane	3-7
cis-1,2-Dimethylcyclohexane	3
AROMATICS (BENZENE AND DERIVATIVES)	
Benzene	0.025-57
Toluene	0.005-129
o-Xylene	0.5-33
m-Xylene	1-61
p-Xylene	1-25
1,2,3-Trimethylbenzene	1-2
1,2,4-Trimethylbenzene	3-15.3
1,3,5-Trimethylbenzene	1.3-11
1,2,3,5-Tetramethylbenzene	1.3-5.3
1,2,4,5-Tetramethylbenzene	1.5-3.9
Ethylbenzene	0.1-22
o-Ethyltoluene	0.7-2.6
m-Ethyltoluene	1.1-13
p-Ethyltoluene	1.1-13
Ethyldimethylbenzene	0.74-2
Styrene	1.5-5
n-Propylbenzene	1-6
Cumene	1-12
p-Cymene	0.12-2
sec-Butylbenzene	4-15
tert-Butylbenzene	2-6

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[a] Compiled from Graedel.[36]

[b] Isoprene is emitted from manmade sources as well as from natural sources (vegetation); terpenes are emitted from natural sources only.

the unpublished EPA data presented later in this section, but are the result of a comprehensive survey of the open literature.

Many of the published detailed studies of organic compounds in the urban atmosphere were conducted in the 1960s. Results of those studies were summarized and discussed in the 1970 criteria document for hydrocarbons.[2] Published data on total levels of organic compounds in urban atmospheres from 1970 through the present are relatively abundant, but most of these data suffer from considerable measurement error because they were obtained by FID instrumentation (Sections 5.2 and 6.2). Nevertheless, FID measurements constitute the most comprehensive published data base on NMHC levels in ambient air. Some statistics derived from FID-measured NMHC are shown for 1967 through 1972 for six cities in Table 6-36.[181]

Because the Los Angeles, California, area has population and traffic density patterns, meteorological characteristics, and emission sources that are uniquely conducive to photochemical oxidant formation, NMHC concentrations have been measured there for many years and these measurements make up the best long-term hydrocarbon data base available. For comparison with earlier data from Los Angeles that were reported in the 1970 criteria document, more recent data from the Los Angles area of the California South Coast Air Basin are reported here. Trends in concentrations of total NMHC for Los Angeles for 1963 through 1972 are shown graphically in Figure 6-6, based on data reported by Trijonis et al.[182] In a separate study of trends in Los Angeles, Mayrsohn and Crabtree looked at long-term changes in concentrations of three "tracer" hydrocarbons--acetylene, propane, and isopentane.[174] These three hydrocarbons are uniquely associated with known sources and thus can serve as tracers that indicate the contributions of those sources to total NMHC concentrations.

TABLE 6-36. FREQUENCY DISTRIBUTIONS FOR 6-TO-9-a.m. NONMETHANE HYDROCARBON CONCENTRATIONS AT CAMP SITES, 1967-1972[181]
(ppm C)

Site	Year	Number of samples	Min.	Percentile[a] 10	20	30	40	50	60	70	80	90	Max.	Arithmetic Mean	Arithmetic Std dev.	Geometric Mean	Geometric Std dev.
Denver, Colo. (060680002A10)	67[b]	29	0.0	0.0	0.3	0.4	0.6	0.9	1.1	1.8	2.3	2.7	5.2	1.3	1.2	0.74	3.69
	68[b]	161	0.0	0.2	0.4	0.6	0.8	1.0	1.1	1.4	1.7	2.7	5.3	1.2	1.0	0.87	3.62
	69[b]	219	0.0	0.0	0.1	0.3	0.5	0.7	0.8	1.0	1.3	1.7	4.9	0.8	0.8	0.50	3.26
	70[b]	231	0.0	0.0	0.2	0.3	0.5	0.6	0.8	1.0	1.1	1.6	5.9	0.8	0.7	0.52	2.96
	71[b]	178	0.0	0.3	0.6	0.7	0.9	1.1	1.3	1.5	1.8	2.4	5.7	1.3	0.9	0.99	2.29
	72	282	0.0	0.1	0.4	0.5	0.7	0.9	1.1	1.3	1.6	2.0	3.9	1.0	0.7	0.74	2.73
Washington, D.C. (090020002A10)	66[b]	250	0.0	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	1.0	1.8	0.5	0.3	0.35	2.56
	68[b]	244	0.0	0.0	0.1	0.1	0.3	0.4	0.5	0.6	0.8	1.1	2.6	0.5	0.4	0.35	2.73
	69[b]	231	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.3	0.3	0.5	2.3	0.2	0.2	0.16	2.27
	70[b]	267	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.3	0.5	0.8	2.0	0.3	0.3	0.19	2.62
	71	279	0.0	0.0	0.0	0.0	0.1	0.1	0.2	0.3	0.5	0.8	3.3	0.3	0.3	0.20	2.64
	72[b]	187	0.0	0.0	0.0	0.0	0.1	0.1	0.3	0.5	0.6	1.1	2.0	0.4	0.4	0.25	2.82
Chicago, Ill. (141220002A10)	68[b]	146	0.0	0.1	0.2	0.4	0.6	0.8	1.0	1.1	1.4	1.8	2.8	0.8	0.6	0.64	2.58
	69	300	0.0	0.0	0.1	0.3	0.5	0.7	0.8	1.1	1.4	1.8	3.6	0.8	0.7	0.54	2.99
	70[b]	220	0.0	0.0	0.0	0.0	0.0	0.0	0.2	0.5	0.8	1.4	4.1	0.5	0.7	0.25	3.20
	71[b]	269	0.0	0.0	0.2	0.3	0.4	0.5	0.6	0.8	1.0	1.4	2.7	0.6	0.5	0.46	2.58
Philadelphia, Pa. (397140002A10)	66[b]	142	0.0	0.0	0.3	0.5	0.6	0.7	0.8	1.1	1.4	1.7	4.2	0.9	0.7	0.64	2.70
	67[b]	260	0.0	0.0	0.1	0.2	0.3	0.5	0.6	0.8	1.1	1.6	5.9	0.7	0.7	0.42	3.11
	68[b]	154	0.0	0.0	0.0	0.1	0.2	0.3	0.5	0.6	0.9	1.6	3.7	0.6	0.7	0.34	3.17
	69[b]	192	0.0	0.0	0.1	0.2	0.3	0.5	0.6	0.7	0.9	1.3	3.7	0.6	0.5	0.42	2.74
	70[b]	264	0.0	0.0	0.1	0.2	0.3	0.4	0.6	0.7	1.0	1.3	2.3	0.5	0.4	0.37	2.90
	71[b]	234	0.0	0.0	0.0	0.1	0.2	0.2	0.4	0.4	0.6	0.9	3.0	0.4	0.4	0.27	2.74
	72[b]	59	0.0	0.0	0.0	0.1	0.3	0.4	0.4	0.6	0.7	1.1	2.4	0.5	0.4	0.31	3.02
Cincinnati, Ohio	68[b]	109	0.0	0.0	0.0	0.1	0.2	0.3	0.4	0.6	0.8	1.4	3.4	0.5	0.6	0.31	3.18
	69[b]	188	0.0	0.0	0.0	0.2	0.2	0.4	0.4	0.5	0.7	1.1	3.1	0.5	0.5	0.32	2.79
	70[b]	99	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.4	2.3	0.1	0.3	0.23	2.22
	71[b]	104	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.9	1.1	2.0	0.6	0.4	0.45	2.37
	72[b]	238	0.0	0.1	0.2	0.3	0.3	0.4	0.4	0.5	0.7	1.0	3.4	0.5	0.4	0.40	2.09
St. Louis, Mo. (264280002A10)	68[b]±	198	0.0	0.0	0.0	0.2	0.4	0.6	0.8	0.9	1.1	1.6	4.4	0.7	0.7	0.44	3.25
	69	292	0.0	0.0	0.1	0.2	0.3	0.4	0.5	0.7	1.0	1.4	3.4	0.5	0.5	0.37	2.83
	70[b]	232	0.0	0.0	0.0	0.1	0.2	0.3	0.4	0.6	0.7	1.1	2.9	0.4	0.4	0.31	2.72
	71	314	0.0	0.0	0.0	0.0	0.0	0.1	0.2	0.3	0.4	0.7	2.5	0.2	0.3	0.19	2.54
	72[b]	235	0.0	0.0	0.0	0.0	0.1	0.2	0.2	0.3	0.4	0.7	1.8	0.3	0.2	0.21	2.42

[a] Concentrations greater than or equal to specified value in indicated percentage of samples.

[b] Yearly standard exceeded.

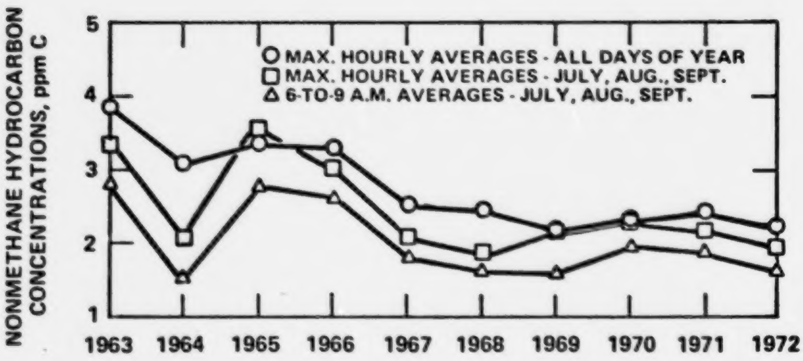

Figure 6-6. Nonmethane hydrocarbon trends in Los Angeles, 1963 through 1972.[182]

Acetylene has been a good indicator of automobile exhaust because, until the widespread use of the catalytic converter, automobiles have been the most significant source of this HC. Isopentane is a major component of both automobile exhaust and of gasoline. Propane, present only in trace amounts in gasoline and auto exhaust, is a major component of natural gas.[174] All three of these compounds have relatively long residence times in the atmosphere and therefore serve as good indicators of the actual quantities in the ambient air of auto exhaust, gasoline vapor, and natural gas, respectively.[174] Table 6-37 shows the 1967 through 1977 concentrations of acetylene, propane, and isopentane at two sites in the Los Angeles area. Mayrsohn et al.[183] measured individual NMHC species and total NMHC at four sites in the Los Angeles area during the smog season (June through September) in 1975. Monitoring was not done concurrently at these Long Beach, El Monte, Azusa, and Upland sites, so that direct comparison of data are not possible. However, the data are useful for indicating the NMHC composition at the respective sites as well as the total NMHC concentrations. These data are presented for C_2 through C_{11} NMHC and for total NMHC in Table 6-38.[183] Although descriptions are not given in this section of the specific methodologies employed in obtaining GC measurements of ambient air samples presented, special note is made on Table 6-38 of the methods used since they differ from the methods used by ESRL, EPA. Mayrsohn et al.[183] measured HC up through C_{18}, whereas ESRL researchers do not commonly attempt to separate or quantify compounds greater than C_{10} because chromatograms often show peaks resulting from column breakdown products that occur at the retention times and temperatures at which compounds $>C_{10}$ are resolved.[184] The miniscule amounts of $>C_{12}$ compounds also complicates their separation, identification, and quantification. The individual concentrations shown in Table 6-38 are for C_2 through C_{11} only, but the total NMHC concentrations include the C_2 through C_{18} compounds.

TABLE 6-37. TRENDS IN 6-TO-9 a.m. CONCENTRATIONS OF INDICATOR HYDROCARBONS AT TWO SITES IN THE CALIFORNIA SOUTH COAST AIR BASIN, 1967 THROUGH 1977[174]
(ppb C)

	Acetylene		Propane		Isopentane	
Year	Azusa	DOLA[a]	Azusa	DOLA	Azusa	DOLA
1967	90	186	87	121	136	302
1968	-	153	-	102	-	280
1969	75	124	113	151	126	214
1870	64	119	91	147	105	245
1971	-	-	-	-	-	-
1972	-	-	-	-	-	-
1973	37	84	56	92	91	169
1974	51	95	71	102	107	175
1975	46	-	63	-	113	-
1976	40	99	53	92	88	185
1977	33	86	56	104	79	154

[a] DOLA = downtown Los Angeles.

TABLE 6-38. MAXIMUM AND AVERAGE 6-TO-9 a.m. NONMETHANE HYDROCARBON CONCENTRATIONS[a] AT FOUR SITES IN CALIFORNIA SOUTH COAST AIR BASIN, JUNE THROUGH SEPTEMBER 1975[183]
(ppb C)

Compound	Long Beach		El Monte		Azusa		Upland	
	Avg.	Max.	Avg.	Max.	Avg.	Max.	Avg.	Max.
Ethane	56	170	114	239	77	122	51	100
Ethylene	26	71	60	118	40	64	40	108
Acetylene	22	63	72	159	46	78	43	88
Propane	72	279	101	212	63	135	48	97
Propylene	10	48	30	69	20	33	14	20
Allene	1	4	4	7	2	4	2	4
Isobutane	36	111	52	176	31	65	30	70
Butane	83	340	111	250	71	143	88	262
Butene-1	3	10	8	16	5	10	4	9
Butene-2	7	19	24	57	15	29	8	16
Isopentane	86	306	171	397	113	233	91	188
Pentane	49	179	87	196	55	110	47	94
Pentenes	2	21	25	93	5	30	2	11
C_6	2	21	167	426	129	282	128	502
C_7	94	394	284	785	202	344	169	441
C_8	80	257	271	762	231	444	157	503
C_9	66	174	200	463	184	1375	111	547
C_{10}	84	342	256	828	294	2149	202	1597
C_{11}	48	224	198	896	229	2933	145	967
Σ NMHC	921	3216	2396	6137	2079	19425	1493	5666
Σ C_2-C_{11}	889	3084	2232	5601	1811	7418	1378	5156

[a] Ethane through pentane separated on Durapak phenylisocyanate porasil-c column. Pentane through xylene separated and quantified by means of SE-30 column. Xylene (C_8) through C_{18} adsorbed on graphitized carbon black, desorbed, and separated and quantified by means of an OV-101 column. GC calibrated with known concentrations of individual components.

Total NMHC data are available for St. Louis from special field studies conducted in 1972 and 1973 by the Environmental Sciences Research Laboratory (ESRL), EPA, at Research Triangle Park, North Carolina.[185] St. Louis, next to Los Angeles, probably is the most-studied city in the United States with respect to air pollution in general and oxidant and its precursors in particular. St. Louis is representative of an urban area having better ventilation characteristics than Los Angeles. Consequently, the ambient air levels of NMHC in St. Louis are considerably lower than those observed in the Los Angeles area. Like Los Angeles, however, the hydrocarbon composition in St. Louis is dominated by automotive-related sources.[186] Total NMHC data are presented in Tables 6-39 and 6-40 for one urban site in 1972 and for one urban site in 1973. These are concentrations in 2-hour samples collected over 24-hours for 6 and 4 days, respectively.

During the 1972 ESRL field study, individual hydrocarbon measurements by gas chromatography (GC) were made at the St. Louis University urban site. Representative data are presented in Table 6-41. These are 24-hour average hydrocarbon concentrations calculated from twelve 2-hour sample measurements on September 13, 1972. Inspection of Table 6-41 easily verifies that methane concentrations far exceed the concentrations of all other hydrocarbons combined. As the table footnote indicates, the value for ethylene is erroneous as the result of contamination from a nearby ozone chemiluminescence monitor. Consequently, the total NMHC concentration is undoubtedly erroneously high. Conspicuous by its absence from this table, benzene is not quantitatively determined by the GC method employed in these and many of the other individual hydrocarbon measurements obtained by ESRL that are reported in this section. (The GC method used by ESRL involves separation of lower-molecular weight aliphatics (C_2 - C_5) on one column, intermediate aliphatics and alicyclics on a second column, and higher-molecular-weight aliphatics, alicyclics,

TABLE 6-39. TOTAL NONMETHANE HYDROCARBON CONCENTRATIONS IN 2-hour SAMPLES MEASURED BY GAS CHROMATOGRAPHY AT URBAN SITE IN ST. LOUIS FOR 6 DAYS, SEPTEMBER 13-25, 1972[a,b]

(ppm C)

Sampling period	Range of values	Average (6 days)
11.00 p.m.-1.00 a.m.	0.416 to 3.847	1.663
1.00 a.m.-3.00 a.m.	0.478 to 4.056	1.466
3.00 a.m.-5.00 a.m.	0.402 to 3.937	1.244
5.00 a.m.-7.00 a.m.	0.486 to 5.491	2.031
7.00 a.m.-9.00 a.m.	0.431 to 6.585	2.125
9.00 a.m.-11.00 a.m.	0.433 to 4.750	1.681
11.00 a.m.- 1.00 p.m.	0.405 to 3.184	1.311
1.00 p.m.- 3.00 p.m.	0.263 to 3.450	1.172
3.00 p.m.- 5.00 p.m.	0.352 to 2.194	1.080
5.00 p.m.- 7.00 p.m.	0.384 to 1.854	0.903
7.00 p.m.- 9.00 p.m.	0.247 to 1.728	0.938
9.00 p.m.-11.00 p.m.	0.242 to 1.912	1.043

[a] St. Louis University site.

[b] Summed from measurements of individual hydrocarbons; ethylene values are excessively high because of contamination, while benzene measurements are absent. Total NMHC, because of erroneously high ethylene data, are accordingly high.

TABLE 6-40. TOTAL NONMETHANE HYDROCARBON CONCENTRATIONS IN 2-hour SAMPLES MEASURED BY GAS CHROMATOGRAPHY AT URBAN SITE IN ST. LOUIS FOR 4 DAYS, JUNE 21-JULY 8,1973[a,b]

(ppm C)

Sampling period	Range of values	Average (6 days)
Midnight-2:00 a.m.	0.467 to 0.858	0.643
2:00-4:00 a.m.	0.270 to 0.842	0.636
4:00-6:00 a.m.	0.199 to 1.112	0.635
6:00-8:00 a.m.	0.341 to 0.860	0.559
8:00-10:00 a.m.	0.465 to 1.567	0.974
10:00-Noon	0.350 to 1.013	0.727
Noon-2:00 p.m.	0.297 to 1.014	0.636
2:00-4:00 p.m.	0.512 to 0.972	0.685
4:00-6:00 p.m.	0.391 to 1.090	0.641
6:00-8:00 p.m.	0.235 to 0.645	0.393
8:00-10:00 p.m.	0.384 to 0.644	0.454
10:00 p.m.-Midnight	0.514 to 0.639	0.572

[a] CAMP site.

[b] Summed from measurements of individual hydrocarbons. Ethylene values within normal range; benzene measurements are absent.

TABLE 6-41. 24-hour AVERAGE HYDROCARBON CONCENTRATIONS MEASURED BY GAS CHROMATOGRAPHY AT URBAN SITE IN ST. LOUIS, SEPTEMBER 13, 1972[a,b], (ppb C)

Compound	24-hr avg. concn.
Methane	5473.8
Ethane	27.3
Ethylene	2212.5[c]
Propane	24.0
Acetylene	24.8
Iso-butane	14.0
n-Butane	57.1
Propylene	6.4
Propadiene	N.D.[d]
Neopentane	N.D.
Iso-pentane	70.8
1-Butene + *Iso*-Butylene	8.2
trans-Butene-2 + Methylacetylene	4.8
cis-Butene-2	1.4
1,3-Butadiene	1.1
n-Pentane	26.4
Pentene-1	2.1
2-Methylbutene-1	3.2
t-Pentene-2	5.3
cis-Pentene-2	1.6
2-Methylbutene-2	5.8
Cyclopentane + 2-Methylpentane	36.0
3-Methylpentane	11.2
4-Methylpentene-2	0.0
Hexane	13.8
Hexene-1	N.D.
2,2-Dimethylpentane	0.7
2,4-Dimethylpentane	6.6
2-Methylpentane	9.1
cis-2-Hexene	0.0
3,3-Dimethylpentane	N.D.
Cyclohexane	N.D.
3-Methylhexane	7.9
2,3-Dimethylpentane	8.8
3-Methylhexane	10.1
1-*cis*-3-Dimethylcyclopentane	1.6
2,2,4-Trimethylpentane	11.6
n-Heptane	5.4
Methylcyclohexane	1.5
Toluene	61.1

TABLE 6-41 (continued)

Compound	24-hr avg. concn.
n-Nonane	5.2
Ethylbenzene	9.0
p-Xylene	7.8
m-Xylene	24.3
o-Xylene	11.1
Isopropylbenzene + styrene	N.D.
n-Decane	13.0
n-Propylbenzene	2.9
m + *p*-Ethylbenzene	6.9
1,3,5-Trimethylbenzene	3.0
tert-Butylbenzene + *o*-Ethyltoluene	1.6
sec-Butylbenzene + 1,2,4-Trimethylbenzene	15.7
Unknown	3.6
1,2,3-Trimethylbenzene	3.6
n-Butylbenzene + *p*-Diethylbenzene	3.6
Σ NMHC	2793.5
Σ NMHC - ethylene	581
Σ Paraffins[e]	362.1
Σ Olefins[f]	64.7
Σ Aromatics[g]	154.2

[a] St. Louis University site.

[b] Gas chromatograph calibrated by standards of individual compounds.

[c] Ethylene concentration not valid; contamination by nearby ozone monitoring[109] system is indicated when the ethylene/acetylene ratio exceeds about 3.

[d] Not detected.

[e] Alicyclics counted with paraffins.

[f] Acetylene counted with olefins.

[g] C_9 unknown counted with aromatics.

and aromatics on a third column. The retention time for benzene is too long on the second column, so that column breakdown products and the diffuse nature of the peak prevent the quantitative measurement of benzene. The separation characteristics and a too rapid elution time for benzene also preclude quantitative measurement on the third column. Measurements of benzene concentrations obtained by other GC methods will be presented separately.)

In a 1974 field study, ESRL obtained total NMHC and individual hydrocarbon data at a rural site in Ohio.[185] The sampling sites for this study were selected as rural ground-level locations downwind of major metropolitan complexes. Although geographically a rural area (Wilmington; McConnelsville; and Wooster, Ohio), this area was found to be affected, as suspected, by transport of polluted urban air masses. Hydrocarbon composition was also found to be influenced by local HC point sources in surrounding communities. Nevertheless, data collected in the Ohio study are probably representative of many such rural areas across the United States.[186] The distribution of total NMHC concentrations (in ppb C) by number of samples is shown in Figure 6-7 for Wilmington and McConnelsville (the latter is located about 100 miles east-northeast of Wilmington).[187]

Individual hydrocarbon concentrations at the Wilmington site were measured by gas chromatography. These data,[185] consisting of 24-hour average concentrations calculated from ten 2-hour and four 1-hour samples, are presented in Table 6-42. Note that the ethylene concentration is quite low. This is significant for a semi-agricultural area, since ethylene is a known phytotoxicant. The low level reflects the relatively light traffic density, since ethylene is emitted mainly in auto exhaust. Though values are reported for acetaldehyde, propionaldehyde, and acetone in Table 6-42, these concentrations are indicative

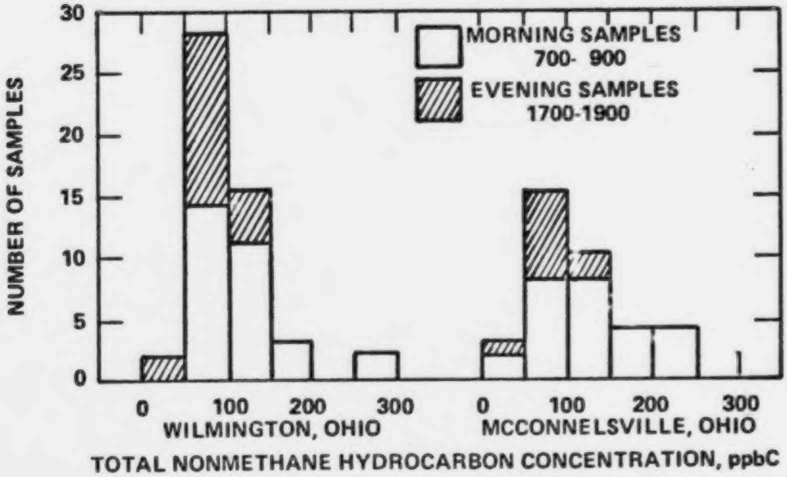

Figure 6-7. Sum of nonmethane hydrocarbon concentrations versus number of samples for two ground sites used in the 1974 Midwest Oxidant Transport Study.[187]

TABLE 6-42. 24-HOUR AVERAGE INDIVIDUAL HYDROCARBON MEASUREMENTS AT WILMINGTON, OHIO, July 18, 1974, DETERMINED BY GAS CHROMATOGRAPHY (ppb C)

Compound	Concn. range	24-hr average concn.
Ethane	7.4 - 13.9	9.9
Ethylene	1.1 - 5.1	2.9
Propane	3.6 - 10.7	6.6
Acetylene	1.6 - 9.2	5.4
Isobutane	1.5 - 7.6	3.9
n-Butane	3.1 - 14.7	8.0
Propylene	0.3 - 1.5	0.7
Isobutylene	0.3 - 2.0	0.8
trans-Butene-2	0.8 - 1.7	1.2
cis-Butene-2	N.D.[a]	-
Butadiene-1,3	N.D.- 0.7	0.1
Isopentane	2.5 - 21.4	8.8
n-Pentane	1.2 - 8.1	3.7
Pentene-1	N.D.	-
2-Methylbutene-1	N.D.	-
trans-Pentene-2	N.D.	-
cis-Pentene-2	N.D.	-
2-Methylbutene-2	N.D.	-
Cyclopentane	0.4 - 5.7	1.6
2-Methylpentane	0.9 - 4.1	2.2
3-Methylpentane	0.7 - 2.8	1.4
4-Methylpentene-2	N.D.- 0.3	0.0
n-Hexane	0.8 - 5.1	2.1
Hexene-1	N.D.- 3.2	0.2
trans-Hexene-3	N.D.	-
2,4-Dimethylpentane	N.D.	-
Methylcyclopentane	N.D.	-
3,3-Dimethylpentane	N.D.	-
Cyclohexane	N.D.	-
2-Methylhexane	N.D.	-
2,3-Dimethylpentane	N.D.	-
3-Methylhexane	N.D.	-
1-*cis*-3-Dimethylcyclopentane	N.D.	-
2,2,4-Trimethylpentane	N.D.	-
n-Heptane	N.D.	-
Methylcyclohexane	N.D.	-
Benzene	0.8 - 4.5	2.3
Toluene	1.0 - 6.8	3.5
Nonane	1.9 - 5.8	3.2
Ethylbenzene	0.3 - 2.3	0.6
p-Xylene	0.3 - 4.8	0.9

TABLE 6-42 (continued).

Compound	Concn. range	24-hr average concn.
m-Xylene	N.D.- 1.0	0.6
o-Xylene	0.2 - 6.1	1.6
n-Decane	0.7 - 2.0	1.2
n-Propylbenzene	0.2 - 1.2	0.3
m,p-Ethyltoluene	N.D.- 0.8	0.4
1,3,5-Trimethylbenzene	N.D.- 1.0	0.1
o-Ethyltoluene	N.D.	-
1,2,4-Trimethylbenzene	0.3 - 2.2	0.8
Unknowns	0.5 - 10.2	5.4
Methane, ppm	1.48 - 2.43	1.6
Total NMHC[b]	42.3 -223.5	101.6
Acetaldehyde	1.3 - 7.5	4.4
Propionaldehyde	N.D.- 11.4	2.6
Acetone	3.0 - 20.7	8.5

---

[a] N.D. = not detected.
[b] Includes aldehydes, acetone, and unknowns.

but not absolute, since oxygenates cannot be measured quantitatively on GC unless calibrated by a specific standard or derivatized prior to measurement. These same data are presented in Table 6-43 by time of day for total hydrocarbons, hydrocarbon classes, and selected oxygenates.

TABLE 6-43. CONCENTRATIONS OF TOTAL NONMETHANE HYDROCARBONS, METHANE, AND SELECTED OXYGENATES IN ELEVEN 2-hour AND TWO 1-hour SAMPLES TAKEN OVER 24 hours, JULY 18, 1974, WILMINGTON, OHIO

	Compound/class, ppb C							
Time	Methane	NMHC[a]	ΣP[b]	ΣO[b]	ΣA[b]	Unknowns	Aldehydes	Acetone
Midnight-2:00 a.m.	1500	71.7	31.8	3.3	20.9	9.0	1.9	4.8
2:00-4:00 a.m.	1520	42.3	24.5	2.9	5.9	2.2	1.8	5.0
4:00-6:00 a.m.	1520	55.4	31.8	4.1	7.1	4.0	4.1	4.3
6:00-8:00 a.m.	1590	65.6	36.5	5.5	8.6	2.8	5.3	6.9
8:00-10:00 a.m.	1590	66.0	40.9	7.0	9.2	1.9	3.2	3.8
10:00 a.m.-Noon	1520	52.7	34.1	3.4	6.8	3.2	2.2	3.0
Noon-2:00 p.m.	1520	128.1	78.5	5.5	10.0	10.2	8.5	15.4
2:00-3:00 p.m.	1480	149.0	91.0	6.3	12.6	9.7	10.2	19.2
3:00-4:00 p.m.	1600	149.7	90.7	5.3	14.7	7.8	10.5	20.7
4:00-5:00 p.m.	2430	223.5	161.6	10.3	14.5	7.3	18.7	11.1
5:00-6:00 p.m.	1500	150.5	93.0	6.3	19.2	9.6	11.8	10.6
6:00-8:00 p.m.	1530	104.3	59.3	4.5	14.8	6.9	7.4	11.4
8:00-10:00 p.m.	2200	84.5	61.5	7.1	6.0	0.5	6.0	3.4
10:00 p.m.-Midnight	1730	78.5	59.1	7.4	5.2	0.5	6.3	N.D.

[a] Includes aldehydes, acetone, and unknowns.

[b] ΣP = total paraffins; ΣO = total olefins; ΣA = total aromatics.

Note the absence in Table 6-42 of the natural hydrocarbons, isoprene (C_5) and the monoterpenes (C_{10}). These compounds can be resolved and identified with the chromatographic columns used in this and subsequently cited studies unless otherwise noted. Isoprene in this chromatographic system would be eluted, if present, between the pentanes and the lower-molecular-weight alicyclics; the monoterpenes would be eluted, if present, after toluene, the xylenes, and ethylbenzene.[110] The absence of natural hydrocarbons from ambient air at this rural site is not atypical of results reported by other researchers for other rural and remote, forested and nonforested sites. Though emission rates for natural hydrocarbons from vegetation have been found to be reasonably high (Section 6.3), ambient air concentrations, even within the canopy of forests, have been found to be low.

Seila,[104] sampling in January, found total NMHC concentrations of about 0.2 ppm C in Jones State Forest, which is primarily a loblolly pine forest, with some oak and sweet gum present, that is located 38 miles north of Houston. Only 2.2 percent of the NMHC concentration, measured in the forest, was natural hydrocarbons, a concentration of about 0.004 ppm C (about 4 ppb C). Arnts and Meeks[188] reported similar concentrations in samples taken from various rural and remote areas during warmer months. They found that total NMHC concentrations generally averaged 40 to 100 ppb C, of which natural hydrocarbons were 10 percent or less (≤ 4 to ≤ 10 ppb C). For rural sites in the East, Ferman[189] reported total NMHC concentrations of 0.1 ppm C or less and terpene concentrations of 0.5 to 2 ppb C. He used a GC method, however, that did not permit unequivocal identification of the terpenes. In his studies, isoprene levels were generally around 2 ppb C. Westberg[110] reported values for natural hydrocarbons in a northern Idaho pine and fir forest of 50 to 1500 parts per trillion C (ppt), with an average of 200 ppt C (0.2 ppb C). Using a specialized mass spectrometric technique in conjunction with GC, Westberg reported the concentrations for natural hydrocarbons in rural ambient air shown in Table 6-44.[110] The effect of distance from the forest is not surprising in view of similar data reported by other researchers (cf. Zimmerman,[119] in Section 6.3). Outside the forest, only benzene and toluene, which are associated with manmade sources, are detectable.

TABLE 6-44. CONCENTRATIONS OF NATURAL HYDROCARBONS IN AMBIENT AIR SAMPLES TAKEN WITHIN AND OUTSIDE A FOREST CANOPY[110]
(ppt C)

Compound	Forest samples, ground level	Outside canopy, 3 ft above ground
Isoprene	580[a]	N.D.[b]
Benzene	610	580
Toluene	190	190
α-Pinene	310	N.D.
β-Pinene	630	N.D.
Δ-3-Carene	370	N.D.

[a] For ppb, multiply by 0.001.

[b] N.D. = Not detectable.

Data representative of a major suburban area were obtained by ESRL in the greater Boston area during the Northeast oxidant transport study in 1975.[185] The individual hydrocarbon data are presented in Table 6-45 as 24-hour average concentrations, in ppb C, that were calculated from twelve 3-hour samples. The data presented here were obtained at sites 10 to 15 miles north and south, respectively, of central Boston. Middleton and Medfield are suburbs north of town; Chickatawbut Hill is an Audubon Society reserve south of town. The qualitative composition is expected to be similar to that in the central city;

the concentrations, however, are lower as a result of dilution.[186] It is also quite possible that the most highly reactive hydrocarbons may have been consumed by the time concentrations were measured 10 to 15 miles out, given the time required for dispersion and transport. The mobile sampling and analysis lab at Chickatawbut Hill was located at the crest of the hill and was surrounded on all sides by trees. Nevertheless, no natural hydrocarbons were detected (α-, β-pinene; Δ-carene; and limonene in Table 6-45).

Data from one final urban area are presented. Houston, Texas, is a good example of an urban area whose atmospheric hydrocarbon burdens are influenced by both automotive and industrial emissions. Houston has a high density of petroleum production and refining activities as well as other major chemical and petrochemical industrial activities. In addition, the shipping channel from Houston to Galveston (another petroleum/industrial city) is responsible for emissions (ship and possibly fugitive emissions from petroleum and other cargo) that influence the ambient air of Houston. The Houston area has a greater number of hydrocarbon-polluting industries than St. Louis or Boston; and certainly more than the rural area represented by Wilmington and McConnelsville, Ohio, even though local influences there included a refinery.[186] Consequently, the Houston area is expected to have a higher proportional contribution from industrial hydrocarbons than would be found in St. Louis or Boston.[186]

The Houston data presented here were obtained at numerous sites in and around the city. A complete analysis of the available data has not yet been made. However, the ranges in total NMHC from day to day and from site to site demonstrate both the effects of local meteorology and the effects of unique local point sources (versus the more homogeneous emissions of auto exhaust and

TABLE 6-45. 24-hour AVERAGE INDIVIDUAL HYDROCARBON CONCENTRATIONS MEASURED BY GAS CHROMATOGRAPHY, BOSTON AREA, 1975 (ppb C)

	Middleton, 8/11/75		Medfield, 8/21/75		Chickatawbut, 8/21/75	
	Avg.	Range	Avg.	Range	Avg.	Range
Ethane	9.7	7.3 - 12.1	3.9	2.0 - 5.2	2.9	2.0 - 4.2
Ethylene	Contam.[a]	Contam.[a]	Contam.[a]	Contam.[a]	5.2	1.2 - 6.8
Propane	11.9	6.9 - 17.4	9.0	1.6 - 21.6	2.7	1.2 - 4.2
Acetylene	10.7	7.5 - 17.6	5.7	2.1 - 10.1	3.9	0.9 - 6.9
Isobutane	9.9	5.8 - 13.1	4.1	1.6 - 6.7	2.8	0.8 - 6.0
n-Butane	22.4	14.6 - 32.4	10.3	3.4 - 15.8	6.2	1.8 - 12.3
Propylene	3.6	2.0 - 6.8	2.3	0.6 - 5.4	1.8	0.4 - 2.8
Isobutylene	3.5	1.3 - 6.8	2.4	1.4 - 4.0	1.8	0.6 - 4.0
trans-Butene-2	1.0	0.2 - 2.2	1.2	0.5 - 1.7	0.7	0.6 - 0.9
cis-Butene-2 + Butadiene	1.8	0.8 - 2.7	1.0	0.5 - 1.9	0.7	N.D.[b] - 1.3
Isopentane	25.6	15.7 - 39.3	15.1	5.6 - 24.1	8.2	2.8 - 13.8
n-Pentane	14.3	9.0 - 22.5	10.5	2.8 - 28.7	4.3	1.5 - 6.4
Pentene-1	0.6	0.3 - 1.3	0.5	0.2 - 0.9	0.2	N.D. - 0.4
2-Methylbutene-1	0.8	0.3 - 1.5	0.7	0.3 - 1.5	0.2	N.D. - 0.6
trans-Pentene-2	N.D.	N.D.	1.0	N.D. - 3.1	N.D.	N.D.
cis-Pentene-2	N.D.	N.D.	0.4	N.D. - 1.7	N.D.	N.D.
2-Methylbutene-2	0.6	N.D. - 1.5	0.9	N.D. - 2.0	0.1	N.D. - 0.8
Acetaldehyde	(6.6)	(3.5 - 8.9)	(2.0)	N.D. - 4.0	(2.4)	1.2 - 3.8
Cyclopentane	6.0	N.D. - 9.3	5.2	1.3 - 8.2	5.4	1.1 - 11.5
2-Methylpentane	10.3	N.D. - 16.3	6.1	2.2 - 11.2	3.8	1.9 - 5.7
3-Methylpentane	6.3	3.9 - 10.7	3.9	1.4 - 6.4	2.6	0.7 - 4.2
4-Methylpentane	N.D.	N.D.	0.1	N.D. - 0.3	0.0	N.D. - 0.2
n-Hexane	6.6	3.9 - 10.8	4.2	1.6 - 6.9	3.5	1.0 - 9.1
Hexene-1	N.D.	N.D.	0.2	N.D. - 0.6	0.0	N.D. - 0.3
Unknown	0.5	N.D. - 0.8	0.4	N.D. - 0.9	0.1	N.D. - 0.4
trans-Hexene-3	0.3	0.2 - 0.7	0.4	N.D. - 0.8	0.1	N.D. - 0.3
2,4-Dimethylpentane	0.9	0.2 - 1.9	0.9	N.D. - 1.8	0.2	N.D. - 0.6
Cyclopentane	4.6	2.8 - 6.2	3.1	1.4 - 5.2	2.4	1.0 - 5.1
cis-Hexene-2	0.1	N.D. - 0.4	0.4	N.D. - 0.9	N.D.	N.D.
Unknown	N.D.	N.D. - 0.2	0.1	N.D. - 0.4	N.D.	N.D.
Propionaldehyde	(N.D.)	(N.D.)	(0.3)	(N.D. - 1.3)	N.D.	N.D.
Acetone	(6.8)	(1.7 - 12.6)	(2.0)	(N.D. - 9.2)	2.0	1.1 - 3.8
3,3-Dimethylpentane	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Cyclohexane	0.8	0.2 - 1.3	0.6	0.3 - 1.0	0.6	N.D. - 1.8
2-Methylhexane	3.2	1.3 - 5.4	2.8	1.1 - 4.8	2.1	N.D. - 4.0
2,3-Dimethylpentane	1.8	0.4 - 3.4	1.4	0.7 - 2.2	1.0	N.D. - 1.8
3-Methylhexane	3.3	1.5 - 6.3	2.8	1.0 - 4.7	2.2	N.D. - 4.2
Unknown	1.6	N.D. - 12.1	0.1	N.D. - 0.6		
1-*c*-3-Dimethylcyclopentane	0.8	N.D. - 1.5	0.4	N.D. - 1.4	0.5	N.D. - 2.1
2,2,4-Trimethylcyclopentane	3.0	1.8 - 5.1	2.3	0.5 - 4.8	2.0	N.D. - 3.0
1-*t*-3-Dimethylcyclopentane	0.3	N.D. - 0.6	0.3	N.D. - 1.0	0.5	N.D. - 1.3
n-Heptane	2.8	0.9 - 4.7	1.9	0.9 - 3.2	2.0	N.D. - 4.4
Methylcyclohexane	1.9	N.D. - 7.3	2.8	1.6 - 4.5	2.1	N.D. - 4.9
Unknown	---	---	1.6	N.D. - 11.1	---	---

TABLE 6-45 (continued).

	Middleton, MA		Medfield, MA		Chickatawbut Hill, MA	
	Avg.	Range	Avg.	Range	Avg.	Range
Toluene	26.5	N.D. - 44.8	21.4	7.9 - 43.6	18.3	8.3 - 41.3
Unknown	1.5	N.D. - 6.5	0.2	N.D. - 0.8	---	---
Unknown	N.D.	N.D.	N.D.	N.D.	---	---
Unknown	N.D.	N.D.	N.D.	N.D.	---	---
n-Nonane	2.8	0.3 - 6.3	0.9	0.2 - 2.2	0.7	0.2 - 1.6
Unknown	0.9	N.D. - 2.9	---	---	---	---
Unknown	0.2	N.D. - 0.6	---	---	N.D.	N.D.
Unknown	0.1	N.D. - 1.0	0.1	N.D. - 0.5	N.D.	N.D.
Unknown	0.2	N.D. - 0.4	0.6	N.D. - 5.0	1.1	N.D. - 3.3
Ethylbenzene	7.2	2.5 - 23.3	5.8	3.2 - 8.7	1.8	0.6 - 3.1
p-Xylene	6.8	2.3 - 19.4	6.6	3.2 - 17.0	3.7	0.4 - 8.5
m-Xylene	21.5	7.2 - 66.4	14.4	N.D. - 24.2	2.2	N.D. - 6.3
Unknown	0.0	N.D. - 0.4	N.D.	N.D.	N.D.	N.D.
α-Pinene	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
o-Xylene	13.2	4.9 - 30.2	6.5	4.8 - 9.6	3.1	1.6 - 4.4
n-Decane	3.9	0.9 - 7.8	1.7	0.5 - 4.4	0.8	N.D. - 1.1
Isopropylbenzene	5.8	1.1 - 23.8	2.0	0.5 - 3.5	0.8	N.D. - 1.7
Unknown	1.5	N.D. - 4.1	0.6	N.D. - 2.1	0.2	N.D. - 1.0
β-Pinene	N.D.	N.D.	N.D.	N.D.	---	---
Unknown	N.D.	N.D.	N.D.	N.D.	---	---
n-Propylbenzene	1.8	N.D. - 4.7	0.8	N.D. - 1.6	0.6	N.D. - 1.1
m,*p*,-Ethyltoluene	6.7	3.0 - 19.3	3.4	1.0 - 6.4	2.0	0.6 - 2.6
Unknown	0.7	N.D. - 3.1	N.D.	N.D.	---	---
Unknown	N.D.	N.D.	N.D.	N.D.	---	---
Δ-3-Carene	N.D.	N.D.	N.D.	N.D.	---	---
1,3,5-Trimethylbenzene	1.5	N.D. - 3.8	0.9	N.D. - 1.6	0.3	N.D. - 0.6
O-Ethyltoluene	1.4	N.D. - 2.9	0.8	N.D. - 1.4	0.3	N.D. - 0.7
1,2,4-Trimethylbenzene	7.3	N.D. - 12.5	5.7	2.0 - 8.6	4.1	2.5 - 5.4
Unknown (Undecane?)	1.4	N.D. - 8.3	---	---	3.7	N.D. - 9.2
D-Limonene	N.D.	N.D.	---	---	---	---

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[a] HC sampler located adjacent to ozone chemiluminescence monitor that employed ethylene; data contaminated.

[b] N.D. Not detected.

fuel evaporation). Variations with time of day demonstrate the effects of ventilation characteristics in respective urban areas. The data for both St. Louis and Houston show that during the 6-to-9 a.m. period hydrocarbon concentrations can be as much as ten times greater than the concentrations during the 1-to-4 p.m. period, even though there is no variation with time of the source emission rates.[186]

Data presented in Table 6-46 demonstrate the diurnal variations in total NMHC (measured by FID) at one site in Houston in 1976. The data show the average concentration and the concentration range for samples measured hourly over 24 hours for 23 days. The concentration during the 6-to-9 a.m. period is about three times higher than that of the 1-to-4 p.m. period.[190]

Additional hydrocarbon data for Houston have been acquired by ESRL in an extensive field study conducted by EPA in conjunction with local and state air pollution agencies. More recent data are still being reduced and prepared for publication. Data for 1973 and 1974 portions of the Houston study are presented in Tables 6-47 and 6-48. Concentrations of the three major classes of hydrocarbons in air samples collected at 19 different sites, in three separate phases of the study, are shown in Table 6-47.[191] Paraffins include the alicyclics for purposes of this tabulation. Detailed gas chromatographic analyses of hydrocarbons in samples collected at three representative sites in Houston in 1973 are presented in Table 6-48.[191] Site 1 is located in the midwestern sector of the city and is representative of the influence of auto exhaust. The site is the farthest of the three from the Houston shipping lanes and is the closest of the three sites to a major traffic artery.[191] The influence of auto emissions is clearly discernible in the concentrations and proportions of ethylene, acetylene, isopentane, 2- and 3-methylpentane, toluene, and the

TABLE 6-46. TOTAL NONMETHANE HYDROCARBON CONCENTRATIONS IN HOUSTON BY TIME OF DAY FOR 23 DAYS, JULY 3-25, 1976, DETERMINED BY FID[190]

(ppm C)

Time of day	Concn. range	Avg. concn.
1:00 a.m.	0.1 - 1.6	0.6
2:00	0.1 - 1.4	0.6
3:00	0.1 - 1.6	0.6
4:00	0.1 - 2.1	0.7
5:00	0.1 - 1.6	0.7
6:00	0.0 - 2.9	0.8
7:00	0.2 - 1.9	1.0
8:00	0.2 - 1.7	1.0
9:00	0.2 - 1.5	0.7
10:00	0.2 - 0.9	0.5
11:00	0.0 - 1.3	0.4
Noon	0.1 - 0.7	0.4
1:00 p.m.	0.1 - 0.7	0.3
2:00	0.1 - 0.8	0.3
3:00	0.1 - 0.6	0.3
4:00	0.1 - 0.6	0.3
5:00	0.1 - 0.9	0.4
6:00	0.1 - 1.3	0.5
7:00	0.1 - 1.3	0.6
8:00	0.1 - 2.0	0.6
9:00	0.3 - 1.9	0.7
10:00	0.2 - 2.4	0.8
11:00	0.2 - 1.3	0.6
Midnight	0.2 - 1.3	0.6

TABLE 6-47. CONCENTRATIONS OF HYDROCARBONS
BY CLASS IN AIR SAMPLES COLLECTED AT 19 SITES[a] IN HOUSTON, 1973
AND 1974, DETERMINED BY GAS CHROMATOGRAPHY[191]
(ppb C)

Date	Sites	Class	Avg. concn.	% of total
September 1973	7 (H01, H03, H04, H06, H07, H08, H09)	Paraffins[b]	298.8	53.6
		Olefins	79.6	14.3
		Aromatics	179.1	32.1
		Total	557.5	100.0
January 1974	7 (H12, H13, H14, H15, H16, H17, H18)	Paraffins	3315.8	69.8
		Olefins	533.1	11.2
		Aromatics	904.4	19.0
		Total	4753.3	100.0
April 1974	5 (H21, H22, H23, H24, H25)	Paraffins	470.9	62.8
		Olefins	136.4	18.2
		Aromatics	143.0	19.0
		Total	750.3	100.0

[a] Sampling sites in traffic tunnels were excluded from this tabulation in order to obtain averages more representative of Houston ambient air.

[b] Paraffins include the alicyclics in this tabulation.

TABLE 6-48. CONCENTRATIONS OF INDIVIDUAL HYDROCARBONS IN AIR SAMPLES COLLECTED IN HOUSTON ON SEPTEMBER 11, 1973, DETERMINED BY GAS CHROMATOGRAPHY[191]

(ppb C)

Compound	Site 1[a]	Site 2[a]	Site 3[a]	Avg. concn.
Ethane	35.1	24.8	21.7	27.2
Ethylene	174.7	30.8	24.5	76.7
Propane	28.0	22.7	19.0	23.2
Acetylene	41.9	8.8	20.7	23.8
Isobutane	41.5	21.4	11.4	24.8
n-Butane	111.3	38.0	29.2	59.5
Propylene	22.5	7.3	9.6	13.2
Isobutylene	20.8	8.4	11.6	13.6
trans-2-Butene	4.1	4.0	4.0	4.0
cis-2-Butene	2.5	1.0	0.0	1.2
1,3-Butadiene	4.1	2.8	4.0	3.6
Isopentane	117.8	42.1	33.5	64.5
n-Pentane	58.5	20.8	20.0	33.1
1-Pentene	4.8	1.7	1.3	2.6
2-Methyl-1-butene	7.1	1.8	1.1	3.3
trans-2-Pentene	9.4	2.9	2.2	4.8
cis-2-Pentene	11.4	7.8	1.3	6.8
2-Methyl-2-butene	7.9	3.1	1.8	4.3
Acetaldehyde	---	---	---	---
Cyclopentane	---	---	---	---
Isoprene	---	---	---	---
2-Methylpentane	52.3	21.7	19.8	31.3
3-Methylpentane	21.8	7.3	8.5	12.5
4-Methyl-2-pentene	0.0	0.0	0.0	0
n-Hexane	30.4	14.3	8.5	17.7
1-Hexene	0.0	0.0	0.0	0
Unknown	0.0	0.0	0.0	0
trans-3-Hexene	---	---	---	---
2,4-Dimethylpentane	7.2	5.0	2.1	4.8
Methylcyclopentane	12.7	10.1	4.7	9.2
cis-2-Hexene	---	---	---	---
Unknown	0.0	0.0	0.0	0
Propionaldehyde	---	---	---	---
Acetone	---	---	---	---
3,3-Dimethylpentane	8.0	0.0	0.0	2.7
Cyclohexane	---	0.0	0.0	0
2-Methylhexane	15.3	0.0	0.0	5.1
2,3-Dimethylpentane	22.5	0.0	0.0	7.5
3-Methylhexane	22.9	0.0	0.0	7.6
1-*cis*-3-Dimethylcyclopentane	---	0.0	0.0	0.0
2,2,4-Trimethylpentane	32.0	0.0	0.0	10.7
1-t-3-Dimethylcyclopentane	---	---	---	---
n-Heptane	16.2	0.0	0.0	5.4

Table 6-48 (continued).

Compound	Site 1[a]	Site 2[a]	Site 3[a]	Avg. concn.
Methylcyclohexane	16.8	0.0	0.0	5.6
Toluene	132.0	35.6	44.2	70.6
n-Nonane	19.9	6.4	7.8	11.4
Ethylbenzene	19.8	6.7	5.3	10.6
p-Xylene	20.0	5.0	5.3	10.1
m-Xylene	86.1	13.0	21.0	40.0
o-Xylene	75.1	8.8	8.4	30.8
Isopropylbenzene	13.5	7.3	---	10.4
n-Decane	20.4	10.1	8.7	13.1
n-Propylbenzene	3.8	4.5	1.3	3.2
p-Ethyltoluene	15.5	10.9	5.8	10.7
m-Ethyltoluene	---	---	---	---
1,3,5-Trimethylbenzene	15.5	0.0	2.6	6.0
o-Ethyltoluene	5.7	9.6	1.5	5.6
1,2,4-Trimethylbenzene	182.9	31.8	6.8	73.8
Unknown	36.6	---	10.1	23.4
1,2,3-Trimethylbenzene	0.0	2.3	0.0	0.8
n-Butylbenzene + *p*-Diethylbenzene	0.0	0.0	0.0	0
m-Diethylbenzene	0.0	0.0	0.0	0
Unknown	0.0	0.0	0.0	0
Methane, ppm	2.01	1.77	1.75	1.84 ppm

[a] See text for site information.

xylenes; all of these are considered to be among the predominating hydrocarbons in auto exhaust.[10] Sites 2 and 3 are in the northeast and southeast sectors of Houston, respectively; they are much closer to the shipping lanes than site 1 and are not close to any major traffic arteries.

More recent data are available from a study conducted by EPA in Houston in September through December 1978 to investigate visibility and photochemical ozone problems in that area.[192] One important aspect of the study was to obtain data on the hydrocarbon composition of ambient air at various locations in the Houston area for subsequent use in a sophisticated photochemical model for ozone. The 1978 investigation of air quality in the Houston area consisted of two individual but complementary studies, the Houston Aerosol Characterization Study (HACS) and the Houston Ozone Modeling Study (HOMS), both of which were the result of a Congressional mandate. The data reported here were collected as part of HOMS.

Grab samples were collected and analyzed by gas chromatography. A total of 109 peaks were seen on the chromatograms, of which unidentified peaks represented 8 to 12 percent of the total NMHC concentration. These unknown compounds may have resulted from sample contamination by outgassing of the sample container, but that is uncertain. The problem is more likely to have affected the sum of unknown aromatics than of paraffins or olefins.[192] It is possible, since a three-column GC procedure was used, that one or more unknown compounds may have been resolved by more than one column, and thus may have been counted twice in the total NMHC concentration.[192] For these reasons, plus the relatively low percentage contribution of the unknowns to the total concentration, the unknowns were excluded from the total NMHC concentration. Only identified compounds are included in the data reported here. Table 6-49 shows the average percentage composition of paraffins, olefin, and aromatics observed at nine HOMS sites. It also includes, for comparison, similar information obtained from two sites in St. Louis in 1972 and 1977.[192]

The results from Houston agree reasonably well with those from St. Louis. Likewise, comparison of these Houston data with those presented in Table 6-47, which were obtained in 1973 and 1974, shows good agreement between the composite averages of the earlier data and the 1978 data from individual sites. It should be noted that Table 6-49 reports only the average composition observed. The composition not only varies from site to site, as shown by these averages, but also fluctuates day to day at each site. The standard deviation reported in Table 6-49 gives an indication of the day-to-day fluctuations that occur. The largest variations are seen in the olefin and aromatic percentages. Variations in the more abundant paraffins are smaller.[192] Overall, the largest variations were seen at sites near industrial areas, where emission patterns are expected to be more variable. The ratio of NMHC to NO_x at the respective sites is included in Table 6-49 and compared with limited data from St. Louis (1977). The data from Houston agree with the limited data from St. Louis except for Houston site 12, which is a site in a "boundary" area located close to Galveston Bay.

The effects of meteorology on hydrocarbon concentrations are demonstrated in Table 6-50, which shows the effects of wind direction on site 03, an urban monitoring site. When the winds were from nonindustrial areas, north to northeast, a higher percentage of the NMHC concentration could be attributed to vehicular tailpipe sources.[192] When the prevailing winds shifted and were from the east and southeast, two effects were observed: (1) the percentage tailpipe emissions decreased; and (2) the total NMHC concentrations increased for both the morning and afternoon time periods.[192]

TABLE 6-49. AVERAGE PERCENTAGE COMPOSITION OF HYDROCARBONS IN AMBIENT AIR AT SELECTED SITES IN HOUSTON (1978) AND ST. LOUIS (1972 AND 1977), 6 TO 9 A.M. PERIOD[192]

Site	Type of site	Paraffins	Olefins	Aromatics	NMHC: NO_x
HOMS					
02	Industrial	63.0 ± 10.9	16.1 ± 5.0	17.8 ± 6.7	15.9 ± 16.6
03	Urban	60.0 ± 4.6	13.5 ± 1.3	23.3 ± 4.1	--
05	Suburban	65.2 ± 5.7	11.1 ± 3.2	21.1 ± 3.2	11.9 ± 6.1
06	Suburban	59.2 ± 4.7	13.9 ± 2.7	23.3 ± 2.0	--
10	Industrial	55.8 ± 11.0	21.4 ± 9.1	20.6 ± 8.7	10.5 ± 1.6
12	Boundary[a]	66.8 ± 6.8	14.2 ± 3.8	16.7 ± 6.3	--
15	Boundary	66.2 ± 3.5	10.3 ± 1.4	20.7 ± 2.8	39.3 ± 13.0
17	Suburban	70.2 ± 12.4	12.4 ± 5.8	16.5 ± 12.0	14.9 ± 9.0
20	Boundary	68.1 ± 7.7	10.0 ± 6.5	19.2 ± 4.4	15.1 ± 8.4
ST. LOUIS					
1972		62.0	11.3	22.7	--
1977		64.0	10.7	24.4	17.0

[a] Between suburban and rural, outside the northern perimeter of Houston.

TABLE 6-50. EFFECT OF WIND DIRECTION ON HYDROCARBON COMPOSITION AT SITE 03, HOUSTON[192]

(ppb C)

Time, CDT	Total NMHC concn.	Paraffins	Olefins	Aromatics
September 18-20, Prevailing winds 90°-104°				
0600-0900	1205.6 (49)[a]	708.5 (40)	194.5 (60)	302.6 (64)
1300-1600	694.7 (40)	377.3 (35)	117.3 (45)	200.1 (45)
September 25-27, Prevailing winds 0°-60°				
0600-0900	1005.3 (60)	557.9 (50)	166.7 (67)	280.7 (68)
1300-1600	504.7 (48)	293.9 (40)	72.7 (64)	139.0 (57)

[a] Percentage of emissions attributable to vehicular emissions is given in parentheses.

Concentrations of two specific hydrocarbons are of special interest because of their adverse welfare and health effects, respectively. Ethylene concentrations in various parts of the country are of particular interest since the 1970 criteria document[2] reviewed the phytotoxic effects of this compound. Concentrations of ethylene are reported for several cities, including Houston, in conjunction with discussion of its phytotoxic properties in the section on welfare effects (Section 6.7).

Concentrations of benzene in ambient air are of concern because of its reported toxicity in humans. As noted earlier in this section, benzene concentration data are sparse among the data obtained from field studies directed toward precursor/oxidant relationships. Since it is considered photochemically nonreactive, and since sampling and measuring it call for specialized techniques, benzene was not measured routinely in the special studies drawn upon in this section. (The data for Wilmington, Ohio, are an exception and do include benzene because of the GC techniques used in that particular study.) Some published data are available, however, that indicate the range of concentrations found in urban air.

In the Wilmington, Ohio, study by ESRL, cited earlier, benzene concentrations ranged from 0.8 ppb to 4.5 ppb over 24 hours (July 18, 1974), with an average of 2.3 ppb. Toluene concentrations measured at the same time ranged from 1.0 ppb to 6.8 ppb, with an average of 3.5 ppb. Westburg's rural air data showed the benzene and toluene concentrations to be 0.58 and 0.19 ppb, respectively.[110] Benzene concentrations in Toronto, Canada, were reported in 1973 by Pilar and Graydon to average 13 ppb C, with a maximum of 98 ppb C.[193] Variations in benzene concentrations with the location of sampling sites were linked with traffic patterns by these authors, who also concluded that automobiles accounted for virtually all benzene contamination and most of the toluene contamination.[193] They attributed the relatively high toluene/benzene ratio in Toronto to the direct evaporation of gasoline, rather than to auto exhaust emissions alone.[193] Toluene/benzene ratios in auto emissions were found in 1966 to range from 1:1 to 2.8:1, with an overall average of 1.8:1.[194] A study in Los Angeles in 1968 showed toluene/benzene ratios there of 1.4:1 to 4:1, with an average of 2.5:1.[26] The ratios in Toronto ranged from 1.5:1 to 4:1, for an average of 2.4:1, which is close to results from Los Angeles. The toluene/benzene ratio from Wilmington, Ohio (a rural area), is 1.5:1. The ratio of toluene to benzene obtained from Westberg's measurements[110] of ambient air immediately outside a forest canopy is 0.33:1, which reflects the effects of residence time, during transport to remote areas, on the disappearance of toluene that results from its greater reactivity relative to benzene. Disparities between auto exhaust ratios and ambient air ratios may indicate other souces of toluene (or benzene) such as gasoline evaporation or solvent losses.[26] Concentrations of benzene in ambient air were measured at four California sites in summer 1975 by Mayrsohn et al.[195] Average concentrations compiled from their data are shown in Table 6-51.

West German researchers[196] determined the effect of reducing the lead content in gasoline, with necessary concomitant increases in aromaticity, on ambient air levels of benzene and toluene. Lead in gasoline was reduced in West Germany from 0.40 g/liter to 0.15 g/liter on January 1, 1976. Data from sixty 15-minute air samples taken in 1975, before the reduction, showed a concentration range for benzene of 7 to 171 $\mu g/m^3$ (2.3 to 57 ppb C), with a

TABLE 6-51. AVERAGE CONCENTRATIONS OF BENZENE IN AMBIENT AIR AT FOUR CALIFORNIA SITES, SUMMER 1975[a]

	Benzene, ppb C			
	Time, PDT			
Site/dates	2:00-5:00 a.m.	6:00-9:00 a.m.	11:00 a.m.-2:00 p.m.	Noon-3:00 p.m.
Azusa, 8/4/75-9/3/75	24.1 (n=16)[b]	29.3 (n-13)[b]	---	24.4 (n = 13)
El Monte, 7/29/75-9/25/75	29.7 (n=37)	40.0 (n=36)	19.9 (n=29)	14.0 (n=3)
Long Beach, 6/10/75-7/16/75	19.8 (n=11)	22.8 (n=7)	15.4 (n=5)	---
Upland, 6/9/75-8/1/75	33.1 (n=15)	38.2 (n=18)	---	23.2 (n=12)

[a] Compiled from Mayrsohn et al.[195]

[b] Number of observations.

mean of 16 ppb C; and a range for toluene of 9 to 355 μg/m^3 (2 to 95 ppb C), with a mean of 100 μg/m^3 (27 ppb C). A series of three studies conducted in 1976 after the reduction in lead content produced the data shown in Table 6-52. The conclusion reached was that increases in aromatics in gasoline did not, in the 6 months immediately following the reduction in lead content, result in higher toluene or benzene levels in ambient air.[196]

TABLE 6-52. MEAN VALUES AND RANGES IN AROMATIC HYDROCARBON CONCENTRATIONS IN WEST GERMANY, JULY 1976[196] (μg/m^3)

Compound	No. samples	Sampling time, min.	Range	Mean	Ratio of means
Benzene	25	30	24 to 84[a]	46	
	12	15	28 to 54	43	
	29	5	17 to 144	55	
Toluene	25	30	57 to 171	101	101/46 = 2.2
	12	15	60 to 111	93	93/43 = 2.2
	29	5	40 to 328	113	113/55 = 2.0

[a] To convert μg/m^3 to ppm, divide by 3175 for benzene and 3780 for toluene.

The NAS document on ozone and other photochemical oxidants[9] depicted graphically the similarities and differences between the hydrocarbon profiles of urban air in the nation as a whole and in the nation with California excluded; and the profiles in auto exhaust and in gasoline. That graph, somewhat modified, is presented as Figure 6-8 to facilitate the same comparison.[9]

6.5 HYDROCARBON-OZONE RELATIONSHIP

The chemical relationship between precursor hydrocarbons and ozone and other photochemical oxidants was summarized in Section 5.1 and updated in Section 6.1. Early efforts to quantify the relationship of hydrocarbons and

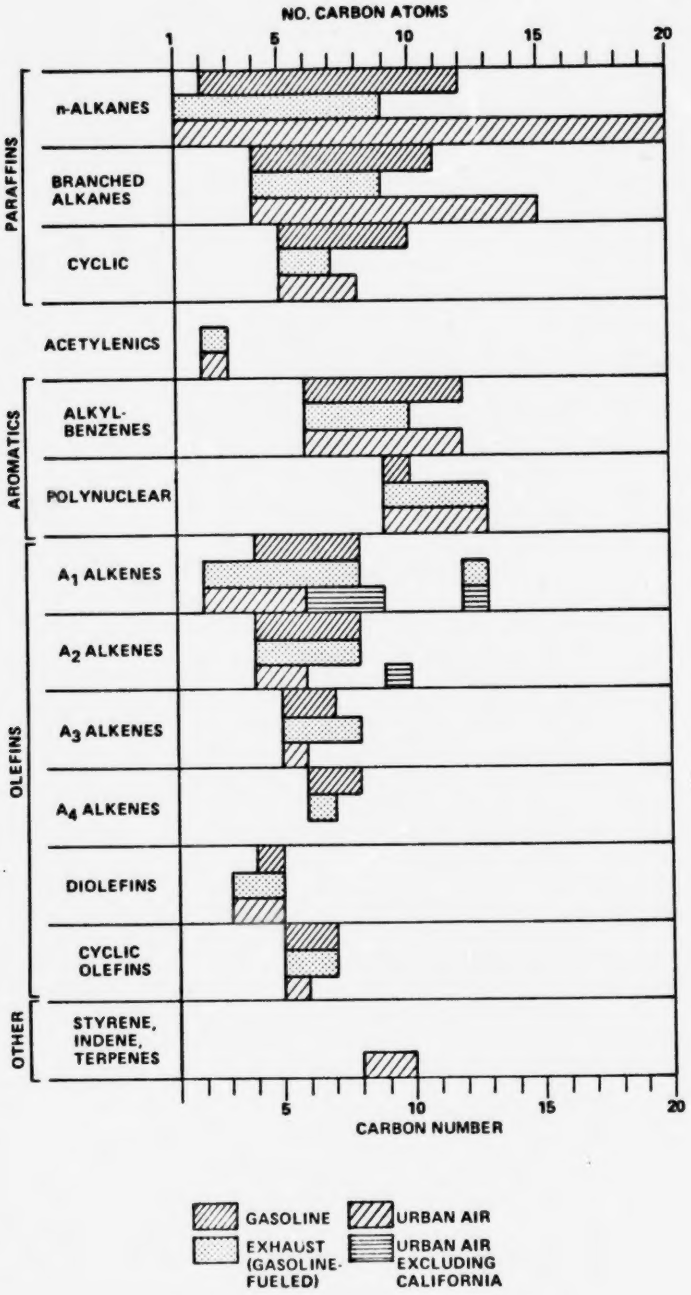

Figure 6-8. Occurrence of gas-phase hydrocarbons, by carbon number, in gasoline, exhaust, and urban ambient air.9

oxidants were summarized in Section 5.5. That section included a brief review of the aerometric data base and of the underlying assumptions that were used to derive the Appendix J model for relating NMHC emissions to oxidant air quality via NMHC ambient air concentrations. The relationship between hydrocarbons and photochemical oxidants was perceived in 1971, when the existing hydrocarbon standard and the Appendix J model were promulgated, to be such that the attainment and maintenance of a given level of ambient air NMHC (an NAAQS) would ensure the attainment and maintenance of the 1971 photochemical oxidant standard. The empirical data that formed the basis of the "envelope curve," or "upper-limit curve," used to derive the 1971 NAAQS for hydrocarbons, and also used to derive the Appendix J model, did not depict an absolute relationship between hydrocarbon ambient air concentrations and resulting oxidant concentrations. Rather, the upper-limit curve was thought to demonstrate that maximum oxidant concentrations in ambient air were primarily a function of 6:00 to 9:00 a.m. concentrations of NMHC in ambient air. Thus, when the oxidant standard was set at 0.08 ppm maximum 1-hour average, not to be exceeded more than once per year, the NAAQS for hydrocarbons was set at 0.24 ppm C, the level shown by the upper-limit curve to be the 6:00-to-9:00 a.m. level that would ensure the production of no more than 0.08 ppm of ambient air oxidant (maximum 1-hour average).

On its promulgation of a new standard for ozone in February 1979, EPA[197] determined that the Appendix J model "no longer represents an acceptable analytical relationship between hydrocarbons and ozone. Appendix J is, therefore, being deleted. EPA will now allow states to use any of four analytical techniques to determine the amount of hydrocarbon reduction necessary to demonstrate attainment of the national ozone air quality standards:..." In taking this regulatory action, EPA has made it clear that the "upper-limit curve," which formed the empirical basis for the Appendix J method, does not adequately describe the relationship between emissions of NMHC and ambient air concentrations of NMHC, and between ambient air concentrations of NMHC and ambient air concentrations of ozone and other photochemical oxidants.

The replacement of the Appendix J method and the setting of the new standard for ozone at 0.12 ppm maximum 1-hour average, not to be exceeded more than once per year, both impact strongly on the existing NAAQS for hydrocarbons. The second fact stated at the beginning of this issue paper must be discussed, at least in a general way, in order to provide an adequate basis for a subsequent regulatory decision on the NAAQS for hydrocarbons. That fact is: According to present knowledge, no fixed level of nonmethane hydrocarbons can be used nationwide to ensure the attainment and maintenance of the ozone NAAQS. In discussing that fact, this section (1) surveys the factors that affect the hydrocarbon-ozone relationship; and (2) briefly discusses the models promulgated by EPA for use in determining reductions needed in precursor hydrocarbon emissions in order to attain and maintain the NAAQS for ozone.

The fact that the original NAAQS was promulgated as a control strategy for the attainment and maintenance of an oxidant standard rather than an ozone standard does not affect this discussion and will not be addressed here. The rationale for promulgation in 1979 of an ozone standard rather than an oxidant standard and the use of hydrocarbon emission reductions as appropriate and effective strategy for the control of ozone and other photochemical oxidants have been fully explained and documented in Air Quality Criteria for Ozone and Other Photochemical Oxidants[7] and in the notice of rulemaking on ozone.[6]

6.5.1 Factors Affecting the Hydrocarbon-Ozone Relationship

As summarized in Sections 5.1 and 6.1, the presence of ozone in ambient air results largely from a series of multiple, complex photochemical reactions involving nitrogen oxides and numerous organic compounds, including hydrocarbons. In the absence of appreciable amounts of organic compounds, resulting levels of ozone remain low as the result of establishment of chemical equilibrium among ozone, nitric oxide, and nitrogen dioxide. In the presence of appreciable amounts of organic compounds, this equilibrium is disturbed and larger amounts of ozone are produced.[10,198] The basic chemistry involved was summarized in simplified form in Sections 5.1 and 6.1. A basic understanding of the chemical relationships among hydrocarbons, nitrogen oxides, and ozone is a prerequisite for the development of techniques that relate precursor emissions to ozone concentrations in ambient air.[7] Three relatively recent documents have presented thorough discussions of the chemical relationships between ozone and its precursors.[7-9] All three also discussed the meteorologic and geographic factors that affect the photochemical formation of ozone, and two of the three reviewed the approaches used to describe quantitatively those relationships for various predictive applications.[7,9] The relative importance of the respective factors--chemical, meteorologic, and geographic--that influence the formation of ozone was evaluated in the cited documents and will not be covered here.

The simple enumeration given in Table 6-53 of the main factors that affect the NMHC-ozone relationship produces a recognition of the complexity of that relationship that is heightened by the realization that these factors are all interactive. Examination of the number and kind of factors that affect ozone production reveals that the relationship between ambient air concentrations of

TABLE 6-53. SOME FACTORS THAT AFFECT THE PHOTOCHEMICAL FORMATION OF OZONE FROM PRECURSORS

Chemical factors

- NMHC and NO_x emissions (starting reactants)
  - Rates/source strength
  - Spatial variations (location, point or area source)
  - Temporal variations (diurnal, seasonal, year-to-year)
  - Species of NMHC emitted
    - Reaction rates
    - Reaction products
  - Stoichiometry (main and side reactions)
  - Ratio of NMHC/NO_x; ratio of NO_2/NO_x
  - Presence of other reactants (including oxygenated HC)
  - Presence of background levels of NMHC and NO_x
  - Presence of scavengers/sinks

Meteorological factors

- Advection
- Mixing heights
- Turbulent diffusion
- Frequency/duration of inversions
- Prevailing winds
  - Direction
  - Speed
- Humidity
- Temperature
- Sunlight intensity
  - Diurnal
  - Seasonal
  - Wavelength distribution

Geographic/topographic

- Longitude and latitude (both affect sunlight intensity, given above)
- Altitude
- Terrain
  - Ventilation characteristics
  - Sinks

---

hydrocarbons and those of ozone cannot, in a given locality much less nationwide, be described by a simple proportionality; that is, hydrocarbon ambient air concentrations are not constant vis-à-vis ozone concentrations. Emissions of NMHC and NO_x and background, or starting, ambient air concentrations, as well as the ratio of NMHC to NO_x, differ from place to place, from city to city. Likewise, the spatial and temporal distribution of these sources of differing strengths varies from city to city.

In addition to those basic chemical factors that affect the photochemical formation of ozone, meteorological factors play an important role. The dependence of ozone concentrations on NO_x and hydrocarbons (and other organics) can be dominated by meteorological conditions.[198] Some of the meteorological variables, such as sunlight intensity and its spectral distribution, directly influence the rates of the ozone-forming photochemical reactions,[7] thereby influencing equilibria among reactants.[198] Geographic location influences photochemical reactions inasmuch as sunlight intensity varies with latitude. Temperature, the net product of geographic and meteorologic factors, directly influences photochemical reactions; summer temperatures, for example, are conducive to ozone formation throughout at least the contiguous United States.[7]

A number of meteorologic and climatic factors other than temperature and sunlight intensity exert major influences on the atmospheric formation of ozone. For example, mixing height and its diurnal variations determine the extent to which local emissions disperse and the extent to which transported ozone and its precursors are likely to affect local ozone concentrations.[198] Atmospheric mixing inhibits the accumulation of precursors and the photochemical formation of ozone and other oxidants.[7] The interaction of locally emitted HC and NO_x with transported pollutants is influenced also by prevailing wind speeds and wind trajectories. Geographic factors that affect the hydrocarbon-ozone relationship are chiefly those that affect the meteorology of an area, such as variations in insolation with latitude. Geography and topography are the main factors in phenomena such as the seabreeze-landbreeze patterns observed in the South Coast Air Basin of California.[7] Topographic influences such as mountains, canyons, and valleys are responsible for unique ventilation patterns that can serve to reduce ozone levels in some areas and to increase them in other areas.[199]

The factors listed in Table 6-53 and surveyed here are not all-inclusive, but they are representative of the complex influences that affect the hydrocarbon-ozone relationship such that the reductions in hydrocarbon emissions needed to attain the NAAQS for ozone will differ from city to city, from season to season, and from year to year.

One factor listed in Table 6-53, the differing reactivities of individual hydrocarbons, is worthy of some detailed discussion inasmuch as it bears upon the question of whether measurements of ambient air concentrations of total NMHC have utility in the determination of needed reductions in hydrocarbon emissions; and because it further emphasizes the added complexity of the oxidant-precursor relationship that is introduced by the observed spatial and temporal variations in the composition of hydrocarbons in the ambient air.

The fact that organic substances, including hydrocarbons, differ widely in their respective reactivities is significant for understanding atmospheric photochemical oxidation processes.[7] This variation in reactivity is also significant because it introduces selective organic compound control as a possible refinement of the practice of controlling all organics to the same extent, irrespective of their reactivity. Variations in reactivity are particularly important conceptually with respect to an ambient air standard for hydrocarbons.

That individual hydrocarbon species participate to differing degrees in the formation of ozone and other secondary products (aldehydes, ketones, organic aerosols, etc.) was acknowledged in the 1970 criteria document for hydrocarbons:

> As a consequence of the differing reactivities of individual hydrocarbons, it is impossible to predict accurately the rate of consumption of hydrocarbons in photochemical air pollution unless the detailed composition of the hydrocarbon component is known or can be estimated. Knowledge of the total concentration of hydrocarbons is insufficient, since two atmospheres having the same total hydrocarbon measurement may contain individual hydrocarbons of very different reactivity and thus exhibit very different rates of hydrocarbon consumption and photochemical air pollution development.[2]

Conceptually, then, a national ambient air quality standard for hydrocarbons is of limited value in controlling photochemical oxidant levels in ambient air. The measurement of total hydrocarbon mass in ambient air does not describe the potential of that atmospheric loading of hydrocarbons for producing ozone or other secondary smog components. Because of the differing reactivities of individual hydrocarbons, ambient air measurements of total NMHC may have limited utility for predicting the impact of hydrocarbon emissions on photochemical oxidant levels, although day-to-day variations in the composition of the hydrocarbon mix within a given city, at a given site, are likely to be much less than the differences that exist between sites in the same city or between different cities.

Reactivity data on hydrocarbons have been obtained from smog chamber studies in which a given hydrocarbon or hydrocarbon mixture is mixed with clean air, NO, and NO_2 at prescribed concentrations and irradiated with artificial sunlight.[7,73] Experimental conditions for such measurements are, to the extent feasible and practical, similar to the conditions typically present in polluted ambient atmospheres. Thus, the reactant concentrations, the intensity and spectral distribution of the radiation, the temperature, and often the relative humidity are comparable to actual summer atmospheric conditions. Because residence time and irradiation time in the atmosphere are prolonged in situations in which the hydrocarbons are transported from the source area, separate hydrocarbon reactivity data must be obtained for simulations of transported air masses. Most available reactivity data are applicable only to urban situations in which the hydrocarbons react for a few hours and cause oxidant pollution in the vicinity of their sources.[7,73]

Reactivity data applicable to urban situations were compiled by Altshuller and are presented in terms of a reactivity classification in Table 6-54.[200] Examination of this table indicates that all hydrocarbons that are precursors to peroxyacyl nitrates, formaldehyde, or aerosols are also precursors to ozone. Consequently, irrespective of their reactivities with respect to the various products listed, control of these ozone precursors should result not only in the abatement of ozone but also in the abatement of these other products as well. As this table indicates, however, not all hydrocarbons are equally reactive in the formation of the respective smog components or effects of smog. Note also that aldehydes, which are both primary and secondary pollutants, are as reactive as many of the hydrocarbons in the production of ozone.

Table 6-54. COMPARISON OF REACTIVITIES OF DIFFERENT TYPES OF ORGANICS[200]

Compound or subclass	Reactivity with respect to designated products or effects, 0 to 10 scale						
	Products				Effects		
	Ozone or oxidant	Peroxyacyl-nitrate	Formaldehyde	Aerosol	Eye irritation	Plant damage	Overall reactivity
C_1-C_3 paraffins	0	0	0	0	0	0	0
Acetylene	0	0	0	0	0	0	0
Benzene	0	0	0	0	0	0	0
C_{4+} paraffins[a]	0-4	0[b]	0[b]	0	0[b]	0	1
Toluene (and other monoalkylbenzenes)	4	ND[c]	2	2	4	0-3	3
Ethylene	6	0	6	1-2	5	+[b]	4
1-Alkenes[d]	6-10	4-6	7-10	4-8	4-8	6-8	7
Diolefins	6-8	0-2	8-10	10	10	0[b]	6
Dialkyl- and trialkylbenzenes	6-10	5-10	2-4	+[e]	4-8	5-10	6
Internally double-bonded olefins	5-10	8-10	4-6	6-10	4-8	10	8
Aliphatic aldehydes	5-10	+[e]	+[e]	ND[c]	+[e]	+[e]	--

[a] Averaged over straight-chain and branched-chain paraffins.
[b] Very small yields or effects may occur after long irradiations.
[c] No experimental data available.
[d] Includes measurements on propylene through 1-hexene, 3-ethyl-1-butene and 2,4,4-trimethyl-1-pentene.
[e] Effect noted experimentally, but data insufficient to quantify.

Results of systematic studies conducted by five groups of researchers* were used by EPA in classifying organics into the three reactivity classes shown in Table 6-55.[7] While this table does not give numerical ratings for the respective organics, it does illustrate the differing reactivities of individual hydrocarbon and other organic species. Furthermore, it demonstrates the differences in reactivity that exist, though not always systematically, between compounds as a result of structural characteristics, including degree and kind of substitution. For example, benzene shows low reactivity, but the insertion of a methyl group results in toluene, which shows high reactivity. Likewise, methanol shows low reactivity, and ethanol is moderately reactive; but 2-ethoxy-ethanol is highly reactive. Partially halogenated paraffins show low reactivity, but partially halogenated olefins demonstrate high reactivity.

These differences in reactivity can be useful in permitting selective or preferential emission control as part of control strategies if the photochemical behavior of a mixture of organic pollutants is consistent with--and can be predicted from--the behavior of the individual components.[7] Overall results of smog chamber studies tend to support the view that the behavior of the mixture can be predicted from the behavior of the components. The main effects on ozone/oxidant production, however, of controlling highly reactive species to a greater degree than moderately or slowly reactive species are: (1) a delay in production of a daily oxidant maximum; and (2) a reduction in the peak oxidant concentrations as a result of increased time for dispersion.[7]

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*Japanese Environment Agency; Bureau of Mines, U.S. Dept. of Interior; General Motors Corp.; Battelle Memorial Institute Laboratories-Columbus; and Shell Oil Co.

TABLE 6-55. CLASSIFICATION OF ORGANICS WITH RESPECT TO OXIDANT-RELATED REACTIVITY IN URBAN ATMOSPHERES[7]

Class I (Low reactivity)	Class II (Moderate reactivity)	Class III (High reactivity)
C_1-C_3 paraffins[a]	*Tert*-monoalkyl benzenes	*Prim*-, *sec*-, monoalkyl benzenes
Acetylene[a]	Cyclic ketones	Dialkyl benzenes
Benzene	Tolualdehydes	Styrene
Benzaldehyde[a]	*Tert*-alkyl acetates[a]	N-Methyl pyrrolidone
Acetone[a]	2-Nitropropane[a]	Partially halogenated olefins
Methanol	C_{4+} paraffins, cycloparaffins[a]	Aliphatic olefins
Isopropanol	Ethanol	Tri-, tetra-alkyl benzene
Tert-alkyl alcohols[a]	*Prim*, *sec* C_{2+} alkyl	Methyl styrene
Methyl acetate[a]	N, N-dimethyl acetamide[a]	Branched alkyl ketones
Methyl benzoate	*n*-alkyl C_{5+}-ketones[a]	Unsaturated ketones
Ethyl amines[a]		Aliphatic aldehydes[a]
N, N-dimethyl formamide[a]		Diacetone alcohol
Perhalogenated hydrocarbons		Ethers[a]
Partially halogenated paraffins		2-Ethoxy-ethanol
Mono, dichlorobenzenes		
Methyl ethyl ketone		

[a] Currently classified as not photochemically reactive under Los Angeles County Rule 66 and similar regulations.

The consequences of "carryover" of organic pollutants to the second day, coupled with transport processes, are under intensive investigation. As yet, few data are available on the reactivities of aged emissions during second-day irradiations. The greater part of unreacted organic precursors will escape the photochemical process during the first solar day and will be transported downwind where, if sufficient NO_x is present on the second day, ozone will be produced from the NO_x and organic precursors. The few reactivity data available for "transport" situations indicate that under transport conditions the effective range of reactivities is narrower than for the urban situation.[7]

6.5.2 Models for Determining Hydrocarbon Emission Reductions

In the years following the 1971 promulgation of the Appendix J method, experience has corroborated the theoretical deficiencies of that method. The Agency has now officially recognized the deficiencies of the Appendix J method by replacing it with other models for determining the HC emission reductions needed to attain the ozone NAAQS. The revisions to 40 CFR, Part 51, that accompanied the notice of promulgation of the new ozone standard in February 1979 stated that:

> ...Appendix J is being replaced by four analytical techniques. States must use one of the four techniques to determine the amount of hydrocarbon reductions necessary to demonstrate attainment of the national ozone standard. The four techniques include: (1) Photochemical dispersion models, (2) Empirical Kinetics Modeling Approach (EKMA), (3) Empirical and Statistical Models, and (4) Proportional Rollback.[197]

EPA further stated in the same notice of promulgation that the use of photochemical dispersion models was specified in certain instances:

> EPA requires that States attempting to demonstrate attainment and maintenance of the revised ozone standard by 1982 without adopting reasonably available control technology (RACT) regulations for large hydrocarbon sources must employ photochemical dispersion modeling.

> The use of other less rigorous analytical techniques are only acceptable in areas where RACT measures are also scheduled for implementation. Where States are unable to demonstrate attainment by 1982, EPA believes any of the models are useful for indicating the magnitude of the ozone problem and for identifying the need for major control programs to be implemented over the next several years.[197]

The techniques prescribed by EPA have as their chief objective the determination of reductions needed in hydrocarbon emissions to attain the ozone NAAQS.

The promulgation of these four models as required options to be used by the states resulted from the efforts of an EPA working group that was formed in 1975 to investigate the viability of alternatives to the Appendix J method.[198] Suggestions made as a result of working group sessions were reviewed periodically by a group of experts outside of EPA. The conclusion reached as a result of these efforts is that it is not possible to recommend a single approach for all applications.[198] The variety of applications, complexity of individual situations, and differences in data availability and resources all preclude use of a single procedure nationwide.[198]

The four models prescribed in February 1979 as alternatives to the Appendix J method are described briefly below.

1. Photochemical Dispersion Models. These are air quality simulation models and are based on the most accurate available physical and chemical principles underlying the formation of ozone.[197] Photochemical dispersion models have the greatest potential for evaluating the effectiveness of oxidant control strategies mainly because (1) the model permits spatial and temporal resolution and (2) it can relate precursor emissions directly to ambient air ozone concentrations via atmospheric dispersion equations and chemical mechanisms. Data requirements for these models may be extensive, however.[198]

2. Empirical Kinetics Modeling Approach (EKMA). This model represents a simpler alternative to the photochemical dispersion models. It includes the use of a kinetic model that represents a detailed sequence, derived from smog chamber data, of the chemical reactions that occur when a mixture of propylene, *n*-butane, and NO_x is irradiated.[198] While retaining some of the vigorous treatment of chemical and physical principles that is characteristic of photochemical dispersion models, it does not require the extensive input data needed for those models.[197]

There are two variations of EKMA. The first involves the use of city-specific ozone isopleths. The second involves the use of a standard set of isopleths in which fixed assumptions have been made about sunlight intensity, atmospheric dilution rate, reactivity of emissions, and diurnal emission patterns. The city-specific approach is preferable because (1) it can be used to evaluate a wider variety of control measures, including measures that are initiated concurrently; and (2) it employs locally unique assumptions about atmospheric dilution rate, sunlight intensity, and diurnal emission patterns.[117] The second advantage is not as crucial as it might appear, however, and using the standard isopleths has the advantage that fewer input data are needed and a computer is not needed.[198]

EKMA makes use of a kinetics model to express maximum afternoon ozone concentration as a function of morning ambient air levels of nonmethane hydrocarbons (NMHC) and NO_x. EKMA is empirical in that it requires the use of observed second-highest hourly ozone concentrations and morning $NMHC/NO_x$ ratios to estimate control requirements.

3. Empirical and Statistical Models. These models are derived from observed relationships between ozone and other variables.[197] Two features of empirical-statistical models are central. First, any one statistical relationship is site-specific. Second, the use of these models is most appropriately limited to applications involving moderate changes from the base control state, since the imposition of drastic changes could appreciably alter the functional relationship that was derived from data observed during the base set of control conditions.[198]

4. Proportional or Linear Rollback. Linear rollback assumes a linear relationship between hydrocarbon emissions and ambient air concentrations of ozone.[121] Other proportional rollback models embody the principle that reductions in emissions are reflected by improvements in air quality, as shown by a curved line or a complex surface that expresses some proportionality relationship.[6] Rollback models work best if the geographic and temporal distribution of emission sources is not changed. The linear rollback model has two chief advantages: (1) it uses aggregated emissions data and (2) it is mathematically simple.[6] It has two chief disadvantages: (1) ideally, it should be applied only to pollutants that do not undergo chemical transformations in the atmosphere; and (2) it does not take into account the dependence of NMHC-ozone relationships on the initial or base period NMHC/NO_x ratio.[198] Linear rollback is less data-intensive than EKMA and is a possible alternative for estimating upper and lower bounds on control requirements for hydrocarbon and other organic precursors.[198]

A limitation of these and other available techniques is that most of these models have received little validation. All of the above techniques, including photochemical dispersion models, must employ simplifications to keep them from being intractable. The accuracy of methods incorporating such simplifications can be determined or at least estimated by verification studies that compare model results with observed data. There are few locations, however, for which the data base is presently adequate for the verification of analytical methods relating precursors and oxidants.[198]

Each of these models has its own characteristic limitations and uncertainties, many of which have not been included here but which are given in detail in other documents.[6,7,73,198] The uncertainties in each model are questions more of degree than of direction. With respect to limitations, however, it should be noted that:

> ...models that relate oxidant to ambient concentrations [of precursors] rather than to emissions [of precursors] are subject to the same validity limitation as the Appendix J method, namely, that the model does not directly relate air quality to precursors. Instead, the direct relationship is between oxidant and the atmospheric dispersion factor.[7,73]

However, in spite of limitations inherent to each of the models briefly described here, they appear to have fewer shortcomings and uncertainties than the Appendix J method. All of the methods indicate that substantial reductions in organic precursors are needed to reduce ozone levels appreciably. Therefore, the four techniques prescribed by EPA can be regarded as approximations[198] that will be useful in estimating hydrocarbon emission control requirements.

The Federal Register issuance[197] that promulgated these four techniques took note of criticisms of the techniques, pointing out that reviewers and commentators have cited various shortcomings. Among the shortcomings listed is the fact that the respective models produce different results. EPA acknowledged in that issuance "that the various techniques do produce different results since different assumptions and different data bases are required for each specific model. Also, EPA agrees that control strategies should be based on the most effective models."[197]

Present information indicates, then, that no one model can be used in all urban areas in the United States for all applications. Thus, present knowledge of available models, along with other scientific evidence, militates against the concept that attainment of a uniform level of NMHC throughout the country is either theoretically or pragmatically sound, from the scientific standpoint, as a means of attaining the ozone NAAQS. This is demonstrated (1) in the complexity and variability of the factors that influence the photochemical formation of ozone; (2) in the fact that no one model can be successfully applied to all situations in all urban areas, coupled with the fact that different models give different results; and (3) the fact that models relating NMHC concentrations, rather than NMHC emissions, to oxidant concentrations really relate those oxidant concentrations to the atmospheric dispersion factor.

6.6 HEALTH EFFECTS

Since promulgation of the hydrocarbon standards in 1971 the direct and indirect effects of hydrocarbons on public health and welfare have been extensively reviewed by EPA in a technical report (1972) entitled, Hydrocarbon Pollutant System Study,[201] and by the National Academy of Science in a monograph (1976) entitled, Vapor-Phase Organic Pollutants.[10] In 1977, NIOSH published a criteria document addressing alkanes (C5-C8).[202] Most recently (1978), the Office of Air Quality Planning and Standards published a document entitled, Assessment of Gasoline Toxicity.[139] This document reviews the various hydrocarbons present in gasoline either as individual compounds, as classes, or collectively as a group of mixed hydrocarbons.

A review of the literature since 1970 reveals once again that hydrocarbons, per se, do not present a significant health hazard in the atmosphere at the present detectable levels. They should be controlled or restricted on the basis of their contribution to photochemical smog and the resultant adverse effects of the smog products. To defend this position properly it seems appropriate to present an up-to-date toxicological evaluation of the hydrocarbon literature addressing each chemical family individually. Components that represent major health hazards are identified and their toxicities are discussed. Because of its objective, this toxicity assessment reviews only the effects associated with environmental exposure to hydrocarbons, either as mixtures (e.g., gasoline, solvents) or as individual compounds, by inhalation.

6.6.1 Aliphatic Hydrocarbons

This class of straight chain or branched hydrocarbons includes the alkanes (saturated), the alkenes (unsaturated, double bond) and the alkynes (unsaturated, triple bond). A number of alkanes (methane, ethane, propane, butane), alkenes (ethylene, propylene), and a single alkyne (acetylene) constitute a group of inert gases and vapors collectively known as "simple asphyxiants." These hydrocarbons, when present in high concentrations in air, act as simple asphyxiants without other significant physiological effects. Any systemic effects that may be observed are thought to be secondary due to the oxygen-replacing capabilities of these gases at extremely high concentrations. No threshold limit values (TLV) have been established for these "inert" substances by the American Conference of Governmental Industrial Hygienists (1979 listing). A TLV is not recommended for each simple asphyxiant because the limiting factor is the available oxygen. The minimum oxygen content should be 18 percent by volume under normal atmospheric pressure (equivalent to a partial pressure, pO_2, of 135 mm Hg). Atmospheres deficient in oxygen do not provide adequate warning and most simple asphyxiants are odorless.

The recent use of isobutane, butane, and propane as substitutes for fluorocarbons in aerosol products raises the question of the potential of these gases to injure humans. Aviado et al.[203] addressed this question in a monograph entitled, Non-Fluorinated Propellants and Solvents for Aerosols. In this monograph the literature was thoroughly reviewed in an attempt to determine whether the mixture of three hydrocarbons (80.4 mol % isobutane, 25 mol % butane, 17.1 mol % propane) is more toxic than each of the individual components. The threshold effective concentration (TEC, based on myocardial and hemodynamic responses) for the hydrocarbon mixture (A-46) was 1.9 percent by volume of air (19,000 ppm) compared to propane (TEC 3.3 percent), isobutane, (TEC 2.0 percent), and *n*-butane (TEC 0.5 percent). The propellant mixture A-46 produces the same pharmacologic effect as other hydrocarbons studied and does not enhance the individual effects of isobutane, butane, and propane. From a health point of view, isobutane is to be preferred over fluorocarbons as a predominant component of aerosol propellant mixtures because it has a higher threshold level for eliciting cardiac arrhythmia.

In general, the simple asphyxiants can be tolerated in high concentrations in inspired air without producing significant physiological effects; however, Reinhardt et al.[204] reported that "aerosol sniffing" of these simple asphyxiants in some cases has sensitized the heart, to the extent that small quantities of epinephrine may lead to ventricular fibrillation and ultimately death through cardiac arrest.

Generally, alkanes from pentane (C_5) through octane (C_8) show increasingly strong narcotic properties. With the exception of respiratory irritation and central nervous system (CNS) depression manifested acutely upon exposure to high vapor concentrations, the C_5 through C_8 aliphatic hydrocarbons are regarded as relatively innocuous. Since exposure to only one alkane is infrequent, NIOSH has recommended a time-weighted average concentration of 350 mg/m^3 as the occupational limit for pentane, hexane, heptane, octane, and total alkanes (mixtures). On a volume/volume (v/v) basis, these concentrations are equal to about 120 ppm pentane, 100 ppm hexane, 85 ppm heptane, and 75 ppm octane. NIOSH also recommends a ceiling limit or maximum acceptable concentration (MAC) of 1800 mg/m^3 for either single hydrocarbons or mixtures, for 15 minutes (about 610 ppm pentane, 500 ppm hexane, 440 ppm heptane and 385 ppm octane). The recommended standard is based on the conclusion that acute intoxication by these alkanes involves a transient central nervous system depression and that chronic intoxication may involve a more persistent effect, polyneuropathy.[202] Polyneuropathy has usually been attributed to n-hexane, but occupational exposures to n-hexane alone have not been described, and the recommended standard is based on the belief that this neuropathy can be caused by other alkanes and their isomers as well. Should sufficient evidence be developed that this is not the case, the TLV limit of 350 mg/m^3 of total alkanes recommended by NIOSH might be considered for upward revision in the case of those alkanes and/or isomers not causing chronic neurological disorders.

The effects of alkane (C_5-C_8) vapor exposure on humans and animals are illustrated in Tables 6-29 and 6-30, respectively.[202]

No studies were found to suggest that any of the volatile aliphatic hydrocarbons are related to carcinogenic, mutagenic, or teratogenic effects in humans or experimental animals; nor is there any reason to suspect that they will be found to produce such effects because these compounds are not chemically related to substances known to have carcinogenic, mutagenic, or teratogenic effects. On the basis of limited bioassays, both alkanes and alkenes have been classified as noncarcinogens, although some of the long-chain (C_{12} or greater) aliphatic hydrocarbons have been implicated as cocarcinogens or tumor-promoters, based on mouse skin-painting experiments.[10] The straight-chain hydrocarbons above octane (C_8) are not sufficiently volatile, however, to warrant serious consideration as vapor hazards at room temperature. In 1976 the American Conference of Governmental Industrial Hygienists (ACGIH) TLV committee imposed a limit of 200 ppm on nonane based on analogy with other members of this series and not on actual data. In 1978, Carpenter et al.[205] established a no ill-effect level for nonane at 590 ppm based on extensive rat inhalation studies. This work was in good agreement with work reported by Nau et al.[206] in 1966. Nonane concentrations commonly found in the ambient air range between 0.0001 and 0.0009 ppm; acceptable workplace exposure levels are 200 ppm (TLV). In view of the low volatility of nonane and its analogy with other aliphatic hydrocarbons, it would appear that this C_9 aliphatic hydrocarbon poses no danger to human health at these ambient levels.

6.6.2 Alicyclic Hydrocarbons

Toxicologically, the alicyclic compounds, as a class, resemble the previously discussed aliphatic hydrocarbons in that they act as general anesthetics and central nervous system depressants with a relatively low order of acute toxicity. The alicyclic compounds (naphthenes), which are present in modern gasolines and gasoline vapors in relatively low concentrations compared to other hydrocarbon components, have not been indicated as hematopoietic toxicants.

Table 6-56. EFFECTS OF ALKANE VAPOR EXPOSURE ON HUMANS[202]

Alkane	Subjects	Exposure concentration and duration	Effects
Pentane	3-6 men and women	Up to 5000 ppm 10 min	No symptoms.
Hexane	3-6 men and women	5000 ppm 10 min	Marked vertigo, giddiness.
Hexane	6 men and women	2500-1000 ppm 10-12 hr/d	Drowsiness in 0.5 hr, fatigue, loss of appetite in some, paresthesia in distal extremities.
Hexane	93 men and women	2500-500 ppm	Sensory impairment in distal portion of extremities, muscle weakness in 13, cold sensation of extremities in some, blurred vision, headache, easy fatigability, anorexia, weight loss at onset of polyneuropathy, muscular atrophy, demyelination and axonal degeneration of peripheral nerves.
Hexane	3-6 men and women	2000 ppm 10 min	No symptoms.
Hexane	3 women	1300-650 ppm 8-10 hr/d 2-10 months	Headache, burning sensation of face, abdominal cramps, numbness, paresthesia, weakness of distal extremities, bilateral foot and wrist drop, absence of Achilles tendon reflexes, fibrillation potentials, decreased conduction time in motor and sensory nerves, denervation-type injury of muscles, numerous neurophathologic changes.
Hexane	11 men and women	1000-500 ppm 3-6 months	Fatigue, anorexia, paresthesia in distal extremities, muscular atrophy.
Hexane	4 men and women	not available	Peripheral neurophathy, reduced motor and sensory nerve conduction velocities, knee-jerk and Achilles tendon reflexes absent, muscular atrophy, diminished sensations of heat and touch, pathologic abnormalities in muscles and nerves.
Heptane	3-6 men and women	5000 ppm 15 min	Marked vertigo, incoordination, hilarity for 30 min.

Table 6-56 (continued).

Alkane	Subjects	Exposure concentration and duration	Effects
Heptane	3-6 men and women	5000 ppm 7 min	Marked vertigo, incoordination of space, hilarity in some.
Heptane	3-6 men and women	5000 ppm 4 min	Marked vertigo, inability to walk straight, hilarity.
Heptane	3-6 men and women	3500 ppm 4 min	Moderate vertigo.
Heptane	3-6 men and women	2000 ppm 4 min	Slight vertigo.
Heptane	3-6 men and	1000 ppm 6 min	Slight vertigo.
Octane	--	--	(No data available.)

Table 6-57. EFFECTS OF ALKANE VAPOR EXPOSURE ON ANIMALS[202]

Alkane	Species	No.	Exposure concentration and duration	Effects
Pentane	Mice	1	129,200 ppm 37 min	Decreased respiration rate, loss of reflexes, death by 37 min of exposure.
Pentane	Mice	4	128,000 ppm 5 min	Irritation, deep anesthesia, respiratory arrest in 1 mouse by 4.75 min of exposure.
Pentane	Mice	1	108,800 ppm 26 min	Lying down, weakened reflexes.
Pentane	Mice		102,000-68,000 ppm 2 hr.	Lying down.
Pentane	Mice	1	91,800 ppm 66 min	Temporary, lying down.
Pentane	Mice	4	64,000 ppm 5 min	Irritation, anesthesia during recovery period.
Pentane	Mice	4	32,000 ppm 5 min	Anesthesia during recovery period.
Hexane	Mice	1	64,000 ppm 5 min	Irregular respiratory pattern, respiratory arrest by 2.5 - 4.5 min.
Hexane	Mice	1	51,120 ppm 9 min	Death after spasms, no narcosis.
Hexane	Mice	1	42,600 ppm 127 min	Loss of reflexes, death.
Hexane	Mice		42,600-34,080 ppm 2 hr	Death.
Hexane	Mice		39,920 ppm 127 min	Death.

Table 6-57 (continued).

Alkane	Species	No.	Exposure concentration and duration	Effects
Hexane	Mice	1	34,080 ppm 123 min	Light narcosis.
Hexane	Mice		32,000 ppm 5 min	Deep anesthesia.
Hexane	Mice		28,400 ppm 2 hr	Lying down.
Hexane	Mice	4	16,000 ppm 5 min	No anesthesia.
Hexane	Mice	4	8000 ppm 5 min	No anesthesia.
Hexane	Mice	7	1000-2000 ppm 6 d/wk, 1 yr	Marked abnormal posture and muscular atrophy and degeneration; in electromyographic tests, fibrillation at rest, complex NMU voltage and high amplitude NMU voltage during movement, and weakened interference waves during strong contractions; increased electrical reaction time; reversal of flexorextensor chronaxy ratio.
Hexane	Mice	6	500 ppm 6 d/wk, 1 yr	Abnormal posture and muscular atrophy.
Hexane	Mice	19	250-2000 ppm 6 d/wk, 1 yr	Higher strength-duration curve with increased concentrations.
Hexane	Mice	6	250 ppm 6 d/wk, 1 yr	Slightly abnormal posture and muscular atrophy; in electromyographic tests, some fibrillation at rest.
Heptane	Mice	4	64,000 ppm 5 min	Respiratory arrest in 3 mice by 3.75 min of exposure.
Heptane	Mice	4	32,000 ppm 5 min	Irregular respiratory pattern.
Heptane	Mice		18,300 ppm 2 hr.	Death in 2 hr.

Table 6-57 (continued).

Alkane	Species	No.	Exposure concentration and duration	Effects
Heptane	Mice	4	16,000 ppm 5 min	No anesthesia.
Heptane	Mice		9760 ppm 2 hr	Lying down.
Heptane	Cats (decerebrated)		24,400-6100 ppm 5 min	Decreased blood pressure during exposure, rapid return to normal during recovery period; initial increased respiration, then decreased.
Octane	Mice	4	32,000 ppm 5 min	Respiratory arrest in 4 mice by 4 min of exposure.
Octane	Mice	4	16,000 ppm 5 min	Respiratory arrest in 1 during recovery period.
Octane	Mice	1	12,840 ppm 185	Decreased respiration rate, death by following day.
Octane	Mice		10,700 ppm 2 hr	Loss of reflexes.
Octane	Mice		8560 ppm 55 min	Narcosis.
Octane	Mice		7490 ppm 2 hr	Lying down.
Octane	Mice		6634 ppm 1 yr	Lying down.
Octane	Mice		5350 ppm 48 min	No narcosis.

These compounds are rapidly metabolized and eliminated in the urine in the form of conjugated glucuronides and sulfates, thus eliminating the chance of increased body burden upon repeated exposure to low atmospheric concentrations. In general, the chronic exposure studies involving animals were very deficient with respect to a dose-response relationship. No occupational or epidemiological evidence was found to indicate that naphthenes have any systemic effects. Unlike the aliphatic hydrocarbons, the degree of toxicity of the alicyclic hydrocarbons does not correlate with structural characteristics (e.g., number of carbon atoms, degree of unsaturation, and amount of branching.

Naphthene vapors at very high concentrations cause irritation of the mucous membranes, with the saturated hydrocarbons generally causing less irritation than the corresponding unsaturated ones. No studies were found regarding the carcinogenic, mutagenic, or teratogenic potential of any alicyclic hydrocarbons.

6.6.3 Aromatic Hydrocarbons

The primary route of exposure to benzene is by vapor inhalation. High concentrations of benzene, like most organic solvents, can cause depression of the central nervous system. Symptoms are acute narcosis, accompanied by drowsiness, vertigo, nausea, unconsciousness, and death. The effects of acute benzene narcosis are usually completely reversible unless the initial severity of exposure causes pathologic changes. Acute poisoning by high concentrations of toluene or the xylenes is uncommon but, like benzene, both toluene and xylene can produce effects on the central nervous system.

The health effects of chronic benzene exposure have been addressed in three recent reviews.[207-209] Benzene exposure by inhalation and other routes is strongly implicated in three pathological conditions; namely, leukemia, pancytopenia, and chromosomal aberrations. The most severe long-term hazard is to the hematopoietic system. Hematopoietic anomalies can affect a number of blood parameters, including erythrocyte count, hemoglobin, mean corpuscular volume of red blood cells, platelet counts, and leukocyte counts. Reportedly, hematologic abnormalities have developed in humans as a result of repeated exposure to benzene concentrations ranging down to 105 ppm and 60 ppm.[210,211] According to Pagnatto's data,[212] suggestive but inconclusive hematologic changes were noted from exposure to benzene concentrations as low as 20 to 25 ppm in rubber-coating plants.

It is now generally agreed that benzene can cause various forms of leukemia which can arise with or without a previous history of aplastic anemia.[213] Knowledge of the carcinogenic potential of benzene has been gained primarily through the experience of human occupational exposure. The exposure data in these studies do not allow a scientific derivation of a dose-response curve. Most studies in which exposure levels were determined involved doses in the range of 100 to 500 ppm, though in some the benzene concentrations were lower. Currently there is no convincing evidence that benzene causes neoplasias, including leukemia, in animals. In animal studies, the most consistent physiological response to benzene has been leukopenia.[202,214,215]

The incidence of benzene-induced chromosomal aberrations in peripheral blood lymphocytes and bone marrow has received considerable attention. Available data from studies in which measurements ranged from 25 to 150 ppm strongly suggest that chromosome breakage and rearrangement can result from chronic exposure to benzene; in at least one study, significant effects were noted at 2 to 3 ppm (time-weighted average).[216] A dose-response relationship has not been demonstrated for benzene-induced chromosome aberrations; however, the apparent lack of relationship may be the result of variations in individual susceptibility.

NIOSH, in recognition of accumulated clinical and epidemiological evidence to the effect that benzene is leukemogenic and a probable cause of other severe systemic toxicity, has recommended a much more stringent standard for occupational exposure to benzene.[217] Since it is not currently possible to establish a safe level of exposure to a carcinogen, NIOSH has recommended that exposure to benzene be kept as low as possible. In accordance with this recommendation, OSHA established an emergency temporary standard for benzene in air at 1 ppm, as an 8-hour, time-weighted, average concentration, with a ceiling level of 5 ppm for any 15 minute period during the 8-hour day.[218] This emergency temporary standard for benzene reduction in the workplace was immediately challenged by industry. In February 1978, this temporary benzene standard was designated permanent;[219] however, this ordered reduction was set aside by a New Orleans Federal Appeals Court the same year. The latter ruled that OSHA cannot legally regulate benzene on the basis of health hazards alone but must include a cost-benefit analysis to determine whether the benefits expected from the revised permanent standard are in proportion to the costs imposed. The Supreme Court on July 3, 1980, agreed with the Appeals Court ruling (5/4 decision) that the benzene rules written by the Labor Department's Occupational Safety and Health Administration were invalid, although the lower court's opinion on cost versus benefit was adopted by only one of the five Justices voting in the majority.

EPA has addressed the effects of benzene exposure in a health document entitled Assessment of Health Effects of Benzene Germane to Low-Level Exposure.[209] In combination with an exposure assessment document entitled Assessment of

Human Exposures to Atmospheric Benzene,[220] the Carcinogen Assessment Group of EPA, using a linear non-threshold model, estimated the leukemic risk at 90 cases per year upon exposure of the general population to ambient atmospheric benzene levels (1 ppb). This amounts to between 0.23 and 1.62 percent of the total leukemia deaths in the United States, based upon 1973 vital statistics.

Toluene (methyl benzene), xylenes (dimethylbenzenes), and trimethylbenzenes are generally much less toxic and volatile than benzene. The primary and most hazardous route of exposure to toluene in the workplace is inhalation. At equilibrium the body retains approximately 50 percent of the inhaled toluene, 20 percent of which is excreted unchanged by the lungs while the remainder is metabolized via the liver to benzoic acid. The majority of benzoic acid (80 percent) is conjugated with glycine and excreted as hippuric acid in the urine. The remaining 20 percent of benzoic acid is conjugated with glucuronic acid in the urine as the glucuronide.

Today there is general agreement in the literature that toluene, unlike benzene, does not affect the hematopoietic system. The myelotoxic effects previously attributed to toluene from early studies are presently judged by updated investigations to be the result of concurrent exposure to benzene as a contaminant. These updated investigations involve both experimental and occupational inhalation exposure to pure toluene. EPA's Carcinogen Assessment Group recently concluded, "there are no adequate studies that describe the carcinogenic potential of toluene."[221]

Effects from toluene have also been reported for other organs, and systems; namely the nervous system, liver, kidney, heart, mucous membrane, immunologic system, and the skin. Like many of the early investigations of the effects of toluene on the hematopoietic system, the reported effects for some of these organs (liver, kidney, heart, peripheral nervous system) are inconsistent and may be attributed to impure toluene and/or inaccurate exposure data. The most sensitive indicators of toluene exposure are a number of symptoms in the central nervous system and in the psychomotor functions. The effects of toluene, however, on the central nervous system are not specific for this aromatic hydrocarbon but typify the responses to other hydrocarbons.

The majority of reported effects have been observed at high exposure levels. Very few observations have been made at exposure levels of 0 to 375 mg/m^3 (0 to 100 ppm). There are no reports on the dose response relationship over an 8-hour workday at these concentration levels. The present threshold limit value for toluene has been established at 100 ppm. A detailed review of the literature regarding the health effects of toluene has been reported by NIOSH[222] and, most recently, by Scandinavian scientists.[223]

No data are available on actual occupational or environmental exposures to xylenes that warrant their consideration as important environmental health hazards. The current xylene standard of 100 ppm was designed primarily to protect workers against the irritating and narcotizing properties of xylene.

6.6.4 Hydrocarbon Mixtures--Gasoline

Inhalation toxicity data based upon human exposure of gasoline vapors are very limited. Inhalation of extremely high concentrations of gasoline vapor can cause narcosis, coma, and sudden death. Death upon acute exposure to gasoline fumes is generally attributed to severe central nervous system depression terminating in respiratory paralysis.[43] Gasoline vapors can sensitize the myocardium to the extent that small quantities of epinephrine may precipitate ventricular fibrillation. This may explain the type of sudden deaths observed in cases of accidental gasoline exposure,[224-228] since the edema observed in these individuals upon autopsy did not appear severe enough to be fatal. This is a reasonable explanation in view of the fact that Chenoweth showed that both gasoline and numerous constituents of gasoline are known to induce ventricular fibrillation in the presence of epinephrine.[229]

Acute inhalation exposures to milder concentrations of gasoline vapor are usually characterized by nonspecific anesthetic or narcotic effects. Symptoms such as headache, vertigo, blurred vision, ataxia, tinnitus, nausea, anorexia, and muscular weakness are not uncommon. Early studies by Drinker et al.[230] demonstrated only slight irritation to the eyes, nose, and throat after human exposure to gasoline for 1 hour. Slight dizziness accompanied the eye irritation at 2600 ppm, while at 10,000 ppm marked intoxication was experienced after 4 to 5 minutes. More recently, a study by Davis et al.[231] revealed no manifestations of intoxication in humans exposed to any of three different unleaded gasolines for 30 minutes at concentrations of 200, 500, and 1000 ppm. The only significant effect reported was eye irritation at the 1000 ppm level. The effects of gasoline vapor on humans are summarized in Table 6-58. Little definitive animal experimentation has been reported to date which assesses the acute toxicity of commonly used gasolines. Machle[43] furnished the only acute toxicity data with respect to animals exposed to gasoline. He reported that gasoline vapor exposures in excess of 10,000 ppm rapidly caused death in most experimental animal species.

Little evidence was found on the health effects of exposure to low concentrations of gasoline vapor over long periods of time. Chronic gasoline toxicity data appear to be limited to a few reports on occupational exposures and some cases of gasoline abuse. Definitive, well-designed epidemiologic studies are not available.

In general, the symptoms of chronic exposure to gasoline vapor are ill-defined. They may consist of fatigue, muscular weakness, nausea, vomiting, abdominal pain, and weight loss. Exposure is also known to have neurological effects which include confusion, atoxia, tremor, paresthesias, neuritis, and paralysis of peripheral and cranial nerves.[232]

Cases of repeated self-induced gasoline intoxication, generally involving higher concentrations of gasoline vapor, could possibly be considered chronic inhalation exposures. Persons engaged in the regular habit of "gasoline sniffing" experience loss of appetite and weight, muscular weakness, and cramps. Other effects reported to result from this practice include abnormal EEG's and organ damage. The greatest hazard associated with chronic gasoline inhalation is exposure to the aromatic hydrocarbons, especially benzene. As previously noted, chronic benzene intoxication can result in severe irreversible systemic effects such as encephalopathy, aplastic anemia, and leukemia. Nothing was found in the literature relating chronic gasoline sniffing with fetal pathological conditions such as liver, kidney, or bone marrow lesions. McDermott and Killiany[233] calculated a TLV for a gasoline based on the hydrocarbon constituents present in gasoline and their respective TLV values. A time-weighted average exposure of 300 ppm over an 8-hour period was estimated to be reasonable along with a ceiling exposure of 1000 ppm for 15 minutes. The TLV was calculated as though benzene has additive effects in the presence of other hydrocarbons. The assumption of additive effects in the calculation of TLVs has been made by ACGIH for all mixtures containing potentially harmful hydrocarbons.[234] The reader is referred to the ACGIH listings of TLVs for a discussion of the basis of TLV calculations for hydrocarbon mixtures.[234]

TABLE 6-58. HUMAN EXPERIENCE: EXPOSURE TO GASOLINE VAPORS

Concentration ppm	Exposure time, minutes	Physiological/sensory effect	Reference
5,000-16,000	5 min	Lethal.	225
10,000	10 min	Nose and throat irritation in 2 min; dizziness in 4 min; signs of intoxication in 4-10 min. Definite intoxication.	Cited in 231
3,000	15 min	Dizziness, nausea.	Cited in 231
2,600	1 hr	Dizziness.	230
2,000	1 hr	Dizziness, mucous membranes irritated and anesthesia.	43
1,000	15 min	Drowsiness, dullness, numbness.	Cited in 231
1,000	1 hr	Dizziness, headache, nausea.	230
1,000	30 min	Eye irritation only.	231
900	1 hr	Slight dizziness, irritation of eyes, nose, and throat.	231
550	1 hr	Eye irritation.	230
500	1 hr	Eye irritation.	43
300-700	18 min	No symptoms.	Cited in 231
160-270	8 hr	Eye irritation.	230

Runion,[235] prior the the Supreme Court decision to overturn the permanent OSHA standard on benzene (1 ppm), re-examined the practical impact of such a standard in relation to gasoline exposure. Gasoline TLVs were calculated using the ACGIH method and incorporating the benzene TLV criterion of 10 ppm, as well as the criterion of 1 ppm. The other constituents of gasoline used in the calculations were estimated on actual ACGIH TLV values. The consequence of a lowered benzene limit on a gasoline TLV is apparent from Figure 6-9.[235] Gasoline containing one percent benzene, for example, had a TLV of 300 ppm, whereas the same gasoline, under the benzene standard which was recently overtuned by the Supreme Court, would have had a TLV of less than 150 ppm.

Recently, Shell conducted a study of service station attendants' exposure to benzene and gasoline vapors in response to the Emergency Temporary Standard originally issued by OSHA. The overall exposure of service station attendants, based on 84 time-weighted average results at seven stations were well below 1 ppm except one exposure at 2.08 ppm. Peak exposures sampled over a 15-minute period did not exceed 1.21 ppm. Attendants' TWA exposures to total gasoline vapor were 114 ppm or less, with measured 15 peak exposures not exceeding 100 ppm during actual filling operations.[236]

The permanent standard on benzene exposure, which was recently (July 3, 1980) ruled invalid by the Supreme Court in a five to four decision, did not attempt to regulate exposures to gasoline in service stations.

6.6.5 Miscellaneous Hydrocarbons

In addition to gasoline, there are many other hydrocarbon mixtures known collectively as "solvents" that are utilized in vast quantities in the United States. The majority of these contain more than one constituent and have boiling ranges varying from less than 10°F to more than 100°F. In general,

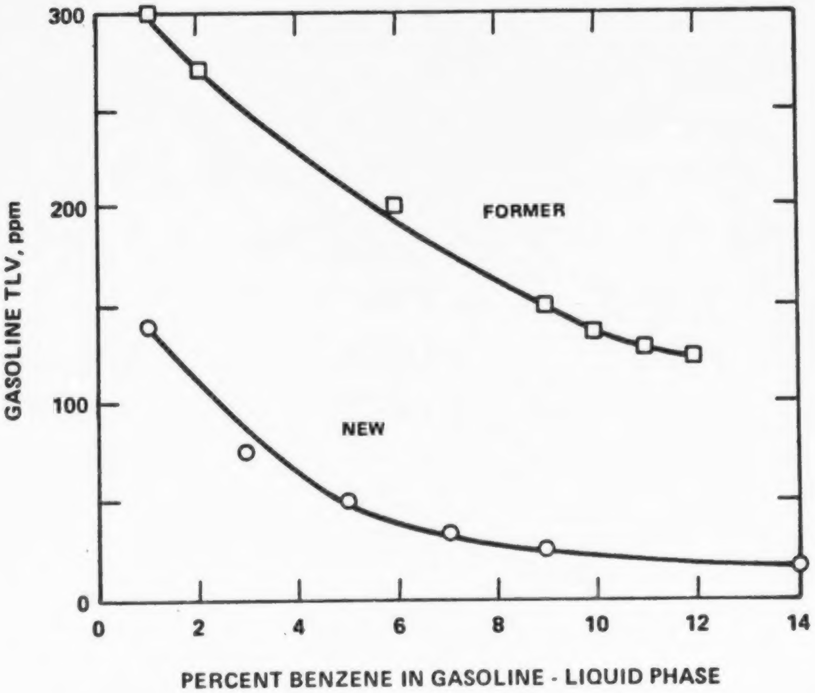

Figure 6-9. Calculated gasoline threshold limit value, reflecting impact of present vs. newly promulgated TLV standard as a function of the liquid volume percent benzene in gasoline.[235]

the hydrocarbon constituents that make up these solvents consist of aliphatics, benzene, alkyl-benzenes, and mono- and dicycloparaffins. The widespread usage and accessibility of these solvents in industry under legitimate conditions lead to potential exposure which may be further compounded by those who intentionally inhale such mixtures for purposes of self-intoxication. Despite the common use of hydrocarbon solvent mixtures, however, there is little published information pertaining to their toxicity. Data up to 1940 have been compiled by Von Oettingen,[237] while information through the 1960s has been summarized by Gerarde[35,238] and by Browning.[239] The majority of these reports suffer from inadequate identification of physical properties and composition of the solvent mixtures tested. Therefore, comparison of results from the various studies is very difficult and application of a study's findings to an immediate solvent exposure situation is difficult.

Since 1965, investigators[206,240,241] have published inhalation toxicity data on animals that are more credible than previous work due to the advent of more sophisticated analytical techniques, which ultimately lead to better characterization of the mixtures tested. To date, the most definitive reports on inhalation toxicology of hydrocarbon mixtures have been published as a series of sixteen articles by Carpenter et al.[242-257] (A standard protocol was followed for 15 different solvent mixtures in evaluation of: (1) their "no-ill-effect" level in rats and dogs; (2) LT_{50} and LC_{50} in rats; (3) central nervous system effects in cats; (4) subacute toxicity in rats and dogs; (5) respiratory irritation in mice, and (6) odor and irritation thresholds in humans.) The suggested hygienic standards for inhalation of these various solvents are based upon inhalation studies with rats and dogs and the sensory response of human subjects. The composition of the hydrocarbon solvent mixtures and the corresponding suggested hygienic standard are summarized in Table 6-59.[205,242-257] Some solvent mixtures (e.g., kerosene) were of such low volatility (low vapor pressure) at 25°C that lethal vapor levels could not be achieved. In these cases, no LC_{50} could be obtained, but the suggested hygienic standard was based upon the sensory response of human subjects at the respective saturated vapor concentrations in air at 25°C.

These studies lend additional support to the concept that the majority of aliphatic, alicyclic, and aromatic hydrocarbons, with the exception of benzene, appear to be relatively nontoxic, even when encountered as mixtures.

6.6.6 Health Effects Summary

Today as in 1970 there are no observed health effects associated with volatile hydrocarbons as a class at ambient levels; however, there are health effects reported at elevated levels for individual hydrocarbons.

Hydrocarbons, strictly speaking, are organic compounds composed of only carbon and hydrogen. There are many other organic compounds which are loosely referred to as hydrocarbons but, in addition to carbon and hydrogen, these compounds contain such elements as the halogens (fluorine, chlorine, bromine, iodine), sulfur, nitrogen, oxygen, etc. Examples of the latter so-called hydrocarbons are perchloroethylene, ethylene dichloride, and ethylene dibromide. The only hydrocarbons considered in the preceding discussion were those that were volatile and contained only carbon and hydrogen. This classification limits the carbon number to approximately twelve and excludes the non-volatile polynuclear aromatic hydrocarbons and the volatile substituted hydrocarbons (e.g., tetrachloroethylene). The volatile hydrocarbons considered can be categorized as aliphatics, alicyclics, and aromatics.

TABLE 6-59. SUGGESTED HYGIENIC STANDARD FOR VARIOUS HYDROCARBON SOLVENT MIXTURES BASED ON INHALATION TOXICITY STUDIES OF ANIMALS AND SENSORY RESPONSE OF HUMAN SUBJECTS[a]

Solvents	Suggested hygienic standard, ppm	Average LC50 rat, ppm	Average LC50 rat, hrs	Constituents of hydrocarbon mixtures, % by volume[b]								
				Paraffins	Cycloparaffins Mono	Cycloparaffins Di	Olefins	Aromatics	Alkyl-benzenes	Benzene	Indans/tetralins	Naphthalene
1) Varnish maker and painters' naphtha	430	3,400	4	55.4	30.3	2.4	-	-	11.7	0.1	0.1	-
2) Stoddard solvent	200[c]	-	8	47.7	26	11.6	-	-	14.1	0.1	0.5	-
3) Rubber solvent	430	15,000	4	41.5	53.6	-	0.1	-	3.4	1.5	-	-
4) Mixed xylenes	110	6,700	4	-	-		-	0.04	99.7	-	-	-
5) "60 solvent"	90	4,900	4	28.8	20.6	0.8	0.3	-	49.5	-	-	-
6) 70 solvent	59[c]	-	8	16.5	12.6	3.1	-	-	57.8	-	6.2	3.8
7) 140 flash aliphatic solvent	37[c]	-	8	60.8	24.5	11.2	-	-	3.0	0.07	0.3	-
8) 80 thinner	100	6,200	4	9.7	18.7	0.2	-	-	70.9	-	0.5	0
9) 90 thinner	430	8,300	4	66.26	0.61		-	-	33 Toluene	0.01	-	-

TABLE 6-59 (continued).

Solvents	Suggested hygienic standard, ppm	Average LC50 rat, ppm	hrs	Constituents of hydrocarbon mixtures, % by volume[a]								
				Paraffins	Cycloparaffins Mono	Cycloparaffins Di	Olefins	Aromatics	Alkyl-benzenes	Benzene	Indans/tetralins	Naphthalene
10) Deodorized kerosene	14[c]	-	8	55.2	32.4	7.6	-	-	3.1	-	0.8	-
11) 40 thinner	25[c]	-	8	35.4	23.3	9.6	0.2	2.9	23.6	0.0	5.0	2.9
12) Toluene concentrate	480	8,800	4	38.69	15.36	-		45.95	45.89 Toluene	0.06	-	-
13) High aromatic solvent	26[c]	-	8	0.3	0.2	0.6	<0.1	89.5	89.5	-	9.2(I)	2.2
14) High naphthenic solvent	380	960	4	29.0	50.6	19.3	-	1.1	0.1 Toluene	-	0.2	-
15) Naphthenic aromatic solvent	380	960	4	24.7	29.1	7.9	-	-	34.2	-	2.8(I)	1.1
16) n-Nonane vapor	590	3,200	4	98.4	unidentified components = 1.6%							

[a] Compiled from references 205, 242-257.
[b] Based on mass spectral analysis.
[c] Saturated vapor concentration in air at 25°C.

All three classes of hydrocarbons, namely the aliphatics, alicyclics, and aromatics, are similar in that they give rise to irritation of the mucous membranes and depression of the central nervous system. Mucous membrane irritation is more pronounced from aromatic vapors compared to equivalent concentrations of aliphatic and alicyclic hydrocarbons. Unlike the aliphatic hydrocarbons, the degree of toxicity of the alicyclic hydrocarbons does not correlate with structural characterisitcs (e.g., number of carbon atoms, degree of unsaturation, and amount of branching). Aliphatic hydrocarbons containing fewer than five carbon atoms are gases at room temperature. The majority of these hydrocarbons, which include methane, ethane, ethylene, propane, propylene, butane, and acetylene, are collectively known as "simple asphyxiants."

Some of these, especially ethylene, propylene, and acetylene, were used as general anesthetics in the past. Any systemic effects observed at extremely high concentrations are considered to be secondary due to the oxygen-replacing capabilities of these gases; however, there are some reports that "aerosol sniffing" of these simple asphyxiants resulted ultimately in cardiac arrests. To date, however, these gases are still considered harmless, physiologically speaking, due to the fact that they are still classified as "simple asphyxiants" by the American Conference of Government Industrial Hygienists (ACGIH) with no assigned threshold limit values.

This is not the case with certain saturated aliphatic hydrocarbons, namely pentane, hexane, heptane, and octane (C-5 to C-8), all of which have been implicated as causative agents in permanent impairment of the peripheral nervous system--namely, toxic polyneuropathy. Based upon the belief that this neuropathy is caused by alkanes other than _n_-hexane, NIOSH recommended a threshold limit value of 350 mg/m^3 for total airborne C-5 to C-8 alkanes, which may in the future be revised upward in the case of those alkanes not causing chronic neurological disorders. This recommended standard by NIOSH lowers the TLV from 500 ppm for hexane, hepane, and octane for each compound to about 100 ppm.

Unlike the aliphatic and alicyclic hydrocarbons, aromatic hydrocarbons have been suspected of causing hematological disorders. There is general agreement, however, from the recent literature that those hematological disorders which have ultimately led to leukemia have been due to benzene alone, and not to any other aromatic hydrocarbons. Knowledge of the carcinogenic potential of benzene has been primarily gained through the experience of human occupational exposure and not through experimental animal studies. Based upon the leukemogenic nature of benzene and its role as the probable causative agent of other severe systemic effects, NIOSH recommended an occupational standard of 1 ppm in place of the previous standard of 10 ppm. OSHA first adopted the 1 ppm standard as an emergency temporary standard and subsequently as a permanent standard. This decision was immediately challenged by industry and ruled invalid by the Court of Appeals of New Orleans. This decision by the lower court was recently upheld by the Supreme Court in its recent five to four ruling against OSHA; the previous 10 ppm standard remains in place.

With the exception of cardiac sensitization, there is little firm evidence that toluene exerts a specific toxic effect on any organ system in experimental animals or in man. Early reports of toluene-induced myelotoxicity have been questioned on the basis that toluene was probably contaminated by benzene in these earlier studies. There is firm evidence, however, that toluene may markedly alter the metabolism of other solvents, especially if they are all oxidized by a common enzyme system in the liver. The present threshold limit value of 100 ppm was designed to protect workers from any CNS depressant effects; however, more recent studies suggest that this situation may be modified by exercise.

Like other hydrocarbons, xylene causes irritation of the mucous membranes and depression of the central nervous system. Individual isomers are apparently similar in narcotic potency/acute potency to mixed xylene vapors. Like that of toluene, reported xylene-induced myelotoxicity was in fact due to contamination with benzene. The present TLV value of 100 ppm was designed to protect workers against minimal irritation and CNS depression.

Many of the health effects associated with individual hydrocarbons are likewise described for exposure to a combination of these components which are commonly found in varying amounts in gasoline and commerical solvents. Health effects observed upon exposure to individual hydrocarbons and to hydrocarbon mixtures are irritation of the mucous membranes, central nervous system depression, and neurological disorders. The majority of the earlier studies addressing the toxicity associated with the inhalation of solvent mixtures lacked creditability because of inadequate characterization of the hydrocarbons present and inaccurate exposure assessments. Since 1965, more reliable data have been published due to the advent of more sophisticated analytical techniques for characterizing mixtures. To date, the most impressive inhalation toxicology studies are those of Carpenter from the viewpoint that the properly designed protocol was followed for all 17 studies, and hygienic standards were suggested based upon both human and animal data.

With the exception of benzene, it appears that aliphatics, alicyclics, and aromatic hydrocarbons are relatively non-toxic even at levels well above those found in the ambient air, whether present as individual compounds or as mixtures.

6.7 WELFARE EFFECTS

Although ethylene as an air pollutant has been reviewed earlier by a number of workers,[258-260] most of the contemporary research and concern has centered around other components of polluted air, such as SO_2, ozone (O_3), peroxyacetylnitrate, CO, fluorides, and particulates. More attention has been focused on the other gases because, unlike ethylene, they have a direct effect on human health and comfort and cause visible vegetation damage in the form of lesions and crop yield reductions.

Ethylene arises from both natural and anthropogenic sources. The former sources include plants (endogenous), soil, natural gas, and burning vegetation, while anthropogenic sources include industries, greenhouses, laboratories, and automobiles. In 1971 Abeles et al.[261] estimated that the total emissions from cars and other manmade sources and activities in the United States was 15 million tons annually, with 93 percent due to the automobile. The contribution from vegetation was estimated to be about 20,000 tons annually or about 0.1 percent of the total emissions. In spite of this constant production of large amounts of ethylene, and occasional ambient measurements of ethylene in urban areas of up to several hundred ppb, the levels in rural areas are still very low (<5 ppb). These low levels existed prior to the introduction of emission controls on mobile and stationary sources; consequently there appear to be natural sinks for the removal of this unsaturated hydrocarbon from the ambient air. These sink processes include oxidation by ozone, gas-phase photochemical reaction with nitrogen dioxide,[262] and aerobic microbial reactions in the soil.[261]

Maximum concentrations of ethylene have been observed in the ambient air of urban areas that are consistent with the increasing traffic density. Ethylene concentrations in urban areas have ranged from <5 ppb up to high values of 700 ppb observed by Abeles and Heggesstad[50] in Washington, DC. In general, these values are peak values and are not truly representative of the majority of observations. This was well demonstrated by Hanan[263] in Denver, where peak values as high as 180 ppb were reported but where the mean levels for three different sampling stations were less than 50 ppb.

Since 1970, EPA has conducted several field studies for the monitoring of total nonmethane hydrocarbon and/or individual hydrocarbons. These include studies at an urban site at St. Louis (1972), rural sites in Ohio (1974), at mixed sites in Houston (1973-1974), and at suburban sites in the Boston area (1975). The data obtained from St. Louis and Boston showed extremely high values of ethylene due to contamination from nearby ozone monitoring systems. The Wilmington, Ohio, site, which is representative of rural areas, showed ethylene levels averaging 1.44 ppb (2.88 ppb C) based on 12 samples taken every 2 hours over a 24-hour period. This is low relative to urban levels, which is important since ethylene has been well established as a phytotoxicant. The data presented in Table 6-60[191] are representative of the concentrations of ethylene at the Houston study sampling sites. Figure 6-10[191] gives the geographical locations of the sampling sites. The majority of these sites are in the ship channel area of Houston and represent the general location of the industrial complex. The maximum concentration measured at the various sites, with the exception of the tunnels, was 166 ppb (332 ppb C) at site H14; the

TABLE 6-60. HOUSTON STUDY ETHYLENE LEVELS[191]

Sampling site code	Location	Concentration	
		ppb	ppb C
9-11-73			
H01	Reagan Road at Euclid Road	87.35	174.7
H02	Baytown Tunnel	479.0	958.0
H03	Pasadena (TACB site)	15.4	30.8
H04	Jacinto City (TACB site)	12.25	24.5
H05	Washburn Tunnel	681.3	1362.7
H06	Industrial Drive	5.0	10.1
H07	Channel View	6.95	13.9
H08	Decker Road	8.4	16.8
H09	Red Bluff	3.15	6.3
1-30-74			
H12	Minden and Dabney Streets	71.5	143.0
H13	Jacinto City (TACB site)	100.95	201.9
H14	Pasadena (TACB site)	131.4	262.8
H15	Queens Road & Revere	165.9	331.9
H16	Jacinto City (TACB site)	165.9	331.9
H17	Pasadena site (TACB site)	74.9	149.9
H18	Downtown Houston	62.15	124.3
4-2-74			
H21	Jacinto City	137.3	274.7
H22	Industrial Drive	39.1	78.2
H23	Jacinto Port Road	19.0	38.0
H24	Deer Park	16.35	32.7
H25	Pasadena	5.3	10.6

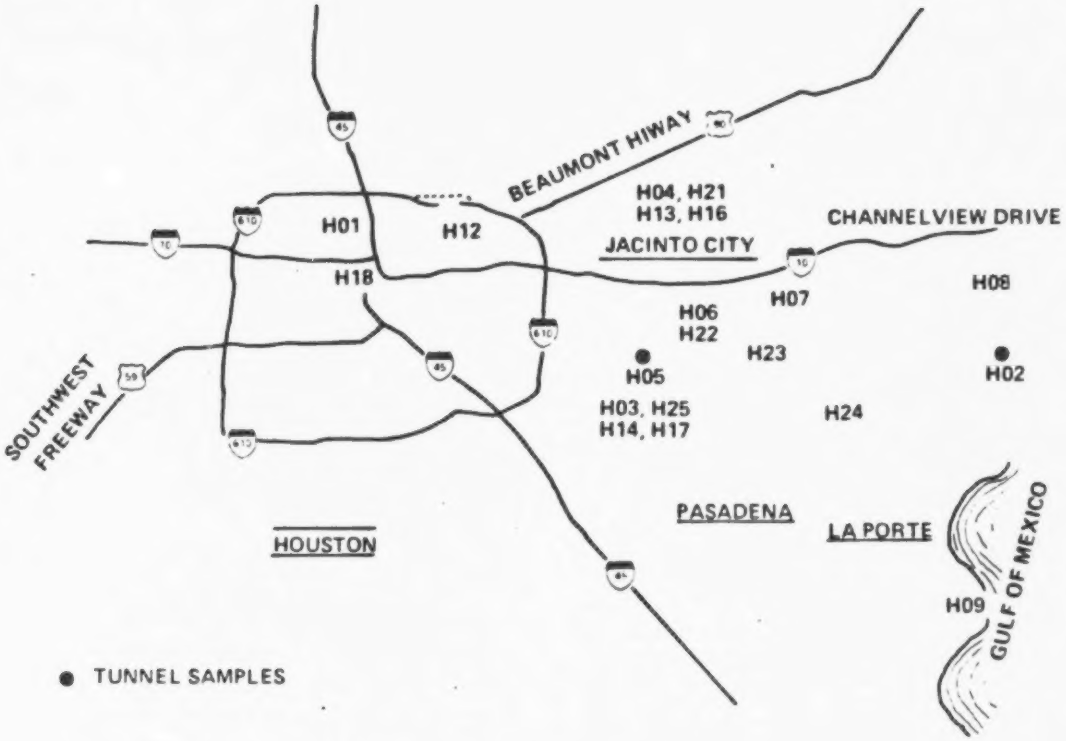
BEAUMONT HIWAY
H04, H21
H13, H16
CHANNELVIEW DRIVE
H01
H12
JACINTO CITY
H18
H08
H07
H06
H22
H23
SOUTHWEST FREEWAY
H05
H02
H03, H25
H14, H17
H24
PASADENA
LA PORTE
HOUSTON
GULF OF MEXICO
H09
● TUNNEL SAMPLES
45
610
10
59

Figure 6-10. Geographic location of the grab sample collection sites, Houston.[191]

lowest concentration measured was 5.0 ppb (10.6 ppb C). The highest average levels of ethylene observed under different meteorological conditions were seen in samples collected at sites H12 through H18, on January 30, 1974. The average ethylene concentration was 110.4 ppb (220.8 ppb C). Since a high pressure system was centered over the Houston area on that date, the nonmethane hydrocarbon (NMHC) levels measured then can be considered to approach the maximum levels expected to occur in Houston.[191] In view of the ethylene contamination from adjacent ozone monitoring instruments, these figures are probably inflated and would average out at less than 100 ppb. In the absence of a nationwide monitoring system, it is extremely difficult to pass judgment on an appropriate mean urban level for ethylene; however, in urban regions that have been monitored, concentrations of 25 ppb are common and 100 ppb levels are not unusual.[50]

Generally, ethylene concentrations required to affect plants in some way, e.g., inhibition of stem or root elongation, should exceed the threshold concentration of 10 ppb. Full or maximum effect is reached at values of 1,000 to 10,000 ppb.[50] Half-maximum effects are observed at 100 to 500 ppb. The effect, however, varies greatly with the duration of exposure to a specific concentration and with plant species.

An effective dosage term (ppb-days) was used by Piersol and Hanan[264] to correlate ethylene concentrations and exposure duration. They reported plant growth inhibition induced by ethylene dosages ranging from 75 to 10,000 ppb-days. Although the highest dosages produced the greatest growth inhibition, 70 to 80 percent of the total maximum inhibition was induced by dosages of around 100 ppb-days.

The effects of urban ethylene production on vegetation have been primarily associated with ornamental plants grown under optimum greenhouse conditions.

The impact of ethylene on welfare has been a problem in certain localities of the country. Ethylene is suspected of causing severe economic problems for individuals involved in the production and retail sale of flowers and crops. In 1962 California adopted an air quality standard for ethylene, namely, 500 ppb for 1 hour and 100 ppb for 8 hours. This standard was designed to protect ornamental flowers that are commercially produced in abundance in California, especially orchids, which are extremely sensitive to ethylene at low levels (100 ppb for 6 hours).[53] Ethylene levels in certain areas of California and Colorado are aggravated by frequent inversions combined with high-density traffic. With the introduction of the catalytic converter on all 1975 model cars and thereafter, the exhaust emissions of ethylene were decreased by a factor of two, from ~ 12 percent to ~ 6 percent of total hydrocarbon emissions. Due to natural sinks and the lack of good monitoring data nationwide, it is not possible to accurately assess pre-1975 and post-1975 ethylene trends. Since 90 percent of nationwide ethylene emissions are associated with urban transportation, it is fairly safe to say that ethylene levels have decreased since 1975 and will continue to do so as more new model cars replace pre-1975 models. This reduction in ethylene levels will hopefully be accelerated by the application of more stringent hydrocarbon emission standards for all 1980 passenger cars, as well as by similar stringent standards for light- and heavy-duty trucks for subsequent model years.

With the exception of plant damage by ethylene, hydrocarbons do not directly affect welfare. Indirectly, however, they are among the pollutants that contribute to the formation of acidic precipitation, which in turn has direct effects on welfare. The direct effects of acid precipitation on public welfare are documented in detail in _Air Quality Criteria for Nitrogen Oxides_.[8]

As a result of the combustion of tremendous quantities of fossil fuels, approximately 50 million tons of sulfur and nitrogen oxides are discharged into the atmosphere annually in the United States. Through a series of complex chemical reactions (see Section 6.1), these gases can be converted into acids which may return to earth as components of either rain or snow. This acidic precipitation, more commonly known as acid rain, may have severe effects on the environment. For example, North American and Scandanavian lakes have become so acidic that they no longer support fish life. More than 90 lakes in the Adirondack mountains of New York State are fishless because acidic conditions have inhibited reproduction. Recent data indicate that other areas of the United States may be vulnerable to similar adverse impacts. Other known effects include: (1) the destruction of monuments and statues and other classical buildings throughout the world; (2) potential damage to crop yield; and (3) possible decreases in the productivity of forests.[8]

6.7.1 Welfare Effects Summary

As early as 1871, hydrocarbons were suspected of causing injury to vegetation; greenhouse plants were found to be highly susceptible. Early investigators suspected other chemicals (e.g., CO, HCN, C_2H_4) as the primary cause of damage. Later studies demonstrated, however, that the principal cause was the gaseous hydrocarbon, ethylene, which was found in illuminating the gas commonly used in greenhouses. Since then, research has demonstrated that ethylene is both an endogenous plant-growth regulator and a serious phytotoxic air pollutant. Dose-response curves have been established for ethylene damage; however, the effect is highly dependent upon concentration, duration of exposure, and plant species.

Although there are natural emission sources of this phytotoxic air pollutant, manmade sources, especially the internal combustion engine, contribute most of the ethylene in ambient air. In general, rural areas have ethylene levels less than 5 ppb. The higher levels observed in urban centers are consistent with traffic density and are highly dependent upon topography and meteorological conditions. This is quite evident in certain areas of California (Los Angeles) and Colorado (Denver) where traffic is dense and inversions are frequent. The ethylene levels and the susceptibility of orchids and other ornamental flowers to ethylene were the prime reason why the State of California adopted an air quality standard for ethylene in 1962. Although ethylene is ubiquitous in nature, its impact on welfare as a phytotoxicant is more severe in certain localities of the country depending on the sensitivity of the plant species grown there. Ethylene is suspected of causing severe economic problems for individuals involved in the production and retail sale of flowers and other crops.

With the advent of the catalytic converter on all new model cars in 1975 and thereafter, ethylene levels should begin to decrease since the internal combustion engine is responsible for greater than 90 percent of ethylene in the ambient air.

Although the welfare effects of hydrocarbons, as a class, are limited to the direct action of ethylene as a phytotoxicant, there are welfare effects indirectly attributed to hydrocarbons. Photochemically reactive hydrocarbons in the presence of sunlight and NO_x react to produce intermediate radicals (e.g., OH, HO_2). These radicals have been implicated in the production of nitric and sulfuric acids from NO_x and SO_x, respectively, through oxidation. Such acids are ultimately returned to earth as components of rain or snow.

This type of acidic precipitation is commonly referred to as "acid rain." In addition to severe impacts on the environment, other effects from acid rain include damage to monuments and other classical structures, reduction in crop yield, and potential decreases in forest productivity.

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